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AFM Study of Phthalocyanine-Based Thin Film Gas Sensor

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1. Introduction

Copper phthalocyanine (CuPc) has been applied to NO_x gas sensors [1]. However, there are still many problems for practical applications; the sensing mechanism is not clarified in detail and the long-term stability is not achieved yet.

We have investigated a relationship between film structure and gas sensitivity to realize the high-sensitive, low working-temperature NO_2 sensor prepared from the α-form CuPc (α-CuPc) thin film. It has been reported [2] that gas sensitivity and electric conductivity are very sensitive to the film structure and morphology. This film microstructure has been controlled by the deposition temperature. Thus, the α-CuPc thin films deposited at room temperature show higher gas sensitivity to NO_2 gas.

In this study, an improvement of the gas sensitivity in a low NO_2 gas concentration range has been attempted by an insertion of higher-sensitive layer between the α-CuPc thin film and the glass substrate. The measured gas sensitivity and gas response characteristics are discussed in relation to the detailed film microstructure analyzed by an atomic force microscopy (AFM).

2. Experimental

The α-CuPc thin films were deposited by the vacuum sublimation method on a glass substrate at room temperature. Vanadil and titanil phthalocyanines (VOPc and TiOPc) were selected as the higher-sensitive materials. They were also deposited at room temperature prior to the deposition of the α-CuPc film in the vacuum of 10^{-4}Pa. Each film thickness was 200 nm with a deposition rate of 0.1nm/s.

The 20 finger interdigitate gold electrodes were vacuum evaporated on the α-CuPc thin films to measure the gas sensitivity to NO_2 gas at a working temperature of 80°C. The conductive current was monitored by using a Keithley 610C electrometer under the dc bias of 10 V in the air and NO_2 gas.

AFM observations were performed with the non-contact mode in air by using JEOL JSTM-4200D.

3. Results and discussion

Gas response characteristics

Gas sensitivity of the VOPc and TiOPc thin films is higher than that of the α-CuPc film in the gas concentration between 100 ppm and 1000 ppm, as shown in Fig. 1. However, the conductive current of the α-CuPc film is higher than those of the VOPc and TiOPc films. This difference is attributed to the difference in the film proper conductivity. The actual flow current is very important for practical sensor devices, i.e. the higher conductive current of the sensor makes a design of peripheral circuits simpler. Therefore, we attempted the insertion of the higher-sensitive VOPc or TiOPc layer between the higher-conductive α-CuPc film and the glass substrate.

The gas sensitivity of the α-CuPc films without and with the higher-sensitive layer is shown in Fig. 2 in the NO_2 gas concentration range from 0.1ppm to 1ppm. Indeed, the sensitivity of the α-CuPc film in this low concentration region is drastically improved by the inserted layer. In particular, the VOPc film is very effective for the improvement, and the actually measured current becomes close to that for the α-CuPc film. Furthermore, the response to 1 ppm NO_2 gas atmosphere for the α-CuPc film with the VOPc layer was reproduced in cycles of NO_2 doping and N_2 dedoping at working temperature of 80°C, as shown in Fig. 3, while the recovery characteristics is insufficient.

It is pointed out in the previous study [2] that the gas sensitivity strongly depends on the film microstructure. Therefore, the above results seem to be closely related to a change of a modification of the film microstrudture.

Film microstructure

It is revealed from the XRD profiles that the α-CuPc film shows only one peak at $2\theta=6.8°$corresponding to an interplane distance of 12 Å, while no peak is detected from the VOPc and TiOPc films. A remarkable reduction in this peak is observed for the α-CuPc film with the TiOPc layer and the peak is disappeared for that with the VOPc layer.

Figure 4 shows AFM images of the α-CuPc, VOPc and TiOPc thin films deposited at room temperature on the glass substrate ((a) ~ (c)), and the α-CuPc thin films deposited on the VOPc and TiOPc layers ((d) and (e), respectively). All the films are composed of small grains ranging from 50 nm to 100 nm in size. The shape and microstructure of the grains are different among the α-CuPc, VOPc and TiOPc films. The microstructure like a V-shape of the VOPc film is reflected in the α-CuPc film deposited on the VOPc film with growing of the grain size, while there is no relation in the microstructure between the TiOPc film and the α-CuPc deposited on the TiOPc film.

It is found from the AFM images that the drastic improvement of the NO_2 gas sensitivity for the α-CuPc film with the VOPc layer is attributed to the same

improvement of the NO_2 gas sensitivity for the α-CuPc film with the VOPc layer is attributed to the same microstructure as the higher-sensitive VOPc film. However, the resulting conductive current is associated with the conductivity of the α-CuPc film.

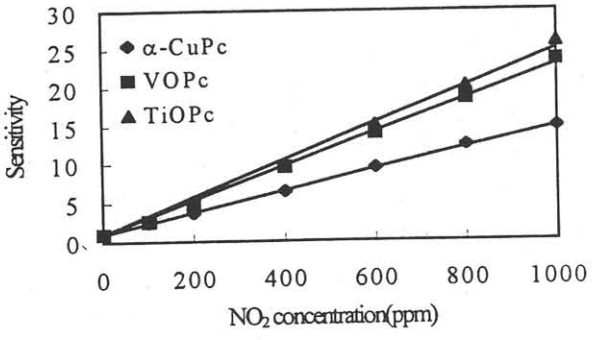

Fig. 1 Dependence of the sensitivity of the α-CuPc, VOPc and TiOPc thin films on the NO_2 gas concentration.

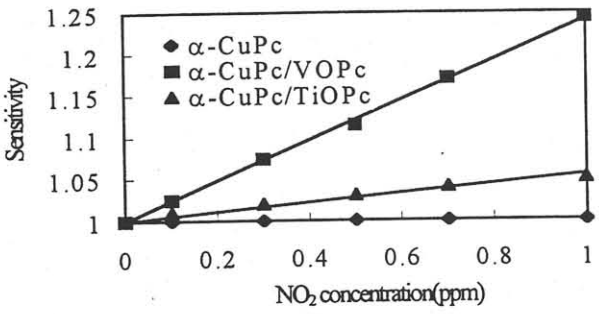

Fig. 2 Dependence of the sensitivity of the α-CuPc thin films without and with the VOPc or TiOPc layer on the low NO_2 gas concentration range.

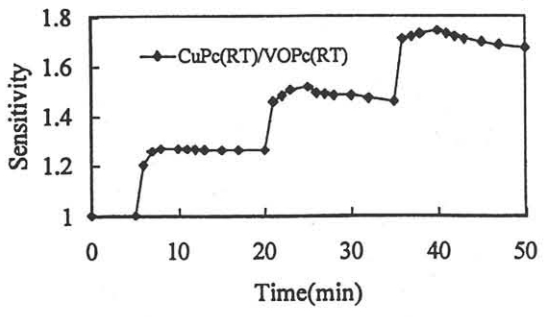

Fig .3 Time response of the α-CuPc/VOPc film in cycles of 1ppm NO_2 doping and N_2 doping.

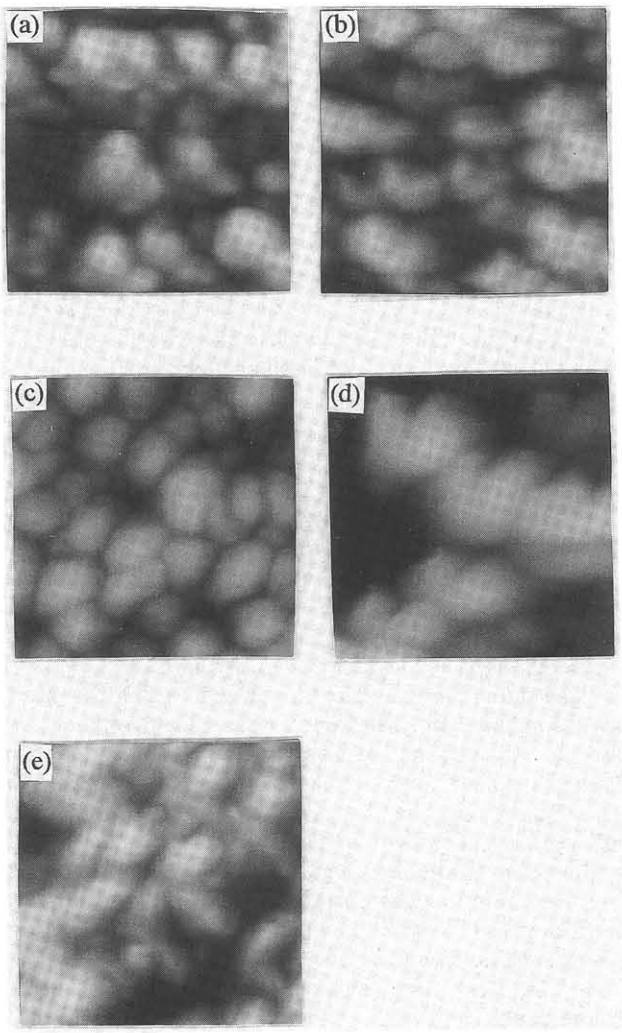

Fig. 4 AFM images (340nmx340nm) of (a) α-CuPc, (b) VOPc, (c) TiOPc, (d) α-CuPc film deposited on VOPc layer and (e) α-CuPc film deposited on TiOPc layer.

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References

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