Novel Attempt to Improve the Sensitivity of Copper-Phthalocyanine-Based Thin Film NO₂ Gas Sensor

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In order to realize high-sensitive, low temperature NO_x gas sensor, thin films of α -form copper phthalocyanine (α -CuPc) have been deposited on a glass substrate by the vacuum sublimation. This paper focuses on a novel attempt to improve the response characteristics of the α -CuPc film-based NO₂ gas sensor through a modification of the film microstructure. The gas sensitivity is remarkably increased especially in a low gas concentration range by an insertion of higher-sensitive layer (vanadil Pc film) between the α -CuPc film and the substrate. The detailed microstructures are investigated by an atomic force microscopy (AFM).

1 INTRODUCTION

Copper phthalocyanine (CuPc) has been applied to NO_x gas sensors for long time.¹⁾ It is known that structure of the CuPc strongly influences its gas sensitivity. For example, the gas sensitivity of amorphous CuPc film was higher than that of the polycrystalline one in the NO₂ gas atmosphere.²⁾ A large variation in NO₂ gas sensitivity was observed for different metal phthalocyanine films.³⁻⁵⁾ Furthermore, the gas sensitivity was increased by substituting the functional groups of the CuPc on its ring structure using the Langmuir-Blodgett (L-B) technique.⁶⁻⁹⁾ However, the structural change requires rigorous control of the sublimation conditions, and the L-B film balance is much complicated than the sublimation apparatus.

We have investigated a relationship between film structure and gas sensitivity to realize a high-sensitive, low working-temperature NO₂ gas sensor prepared from the α -form CuPc (α -CuPc) thin film. It has been reported¹⁰⁾ that the gas sensitivity and the electric conductivity are very sensitive to the film microstructure and morphology, and the film microstructure is controlled by a deposition temperature. As a result, the α -CuPc thin films deposited at room temperature show the higher gas sensitivity to NO₂ gas.

In the present study, we have proposed a novel, simpler method to improve further the gas sensitivity of α -CuPc thin film-based NO₂ gas sensor, especially in a low gas concentration range. This method includes an insertion of the higher-sensitive layer between the α -CuPc thin film and the glass substrate. 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 the glass substrates at room temperature in the vacuum of 10^{-4} Pa. Vanadil phthalocyanine (VOPc) was selected as a higher-sensitive material and also deposited at room temperature prior to the deposition of the α -CuPc film. Both materials, were sublimed at between 450 °C and 500 °C. When the double-layered film was formed, the VOPc film was exposed to air to change the source material from VOPc to α -CuPc. Each film thickness was monitored by quartz oscillator to be 200 nm with a deposition rate of 0.1 nm/s. The glass substrate was cleaned in advance with distilled water and ethanol.

The 20-finger interdigitated gold electrodes were vacuum evaporated on the α -CuPc thin films to measure an electric conductivity in NO₂ diluted N₂ gas and N₂ reference gas. Effect of ambient humidity can be decreased by operating the

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element at elevated temperature¹¹⁾ and the effect has been eliminated completely for the α -CuPc thin film operated at 80 °C.¹⁰⁾ Therefore, the working temperature is kept at 80 °C for various Pc films in the present study. The NO₂ gas is diluted in N₂ gas for various concentrations, then injected (with a flow rate 0.86 ℓ /min for one minutes) into an acrylic cell (volume of 0.86 ℓ) containing the sample. The conductive current was monitored by using a Keithley 610 C electrometer under the dc bias of 10 V. The current in μ A order can be obtained with this bias voltage. Details of the measurement are illustrated in Fig. 1.

The film microstructure was characterized by using the X-ray diffractometer (RIGAKU RAD-2 A) with a Ni-filtered Cu-K α radiation and the AFM (JEOL JSTM-4200 D) with a non-contact mode in air.

3 RESULTS AND DISCUSSION

Figure 2 shows the gas sensitivity for α -CuPc, VOPc and α -CuPc deposited on VOPc (α -CuPc/VOPc) thin films in the NO₂ gas concentration range upto 1000 ppm. The gas sensitivity is defined as a ratio of the measured current in NO₂ gas to the current in N₂ reference gas. The gas sensitivity has a tendency to saturate within 5 min at each gas concentration. Thus the current is measured after the 5-min exposure to the gas. The VOPc single film has the higher gas sensitivity than the α -CuPc single film, while the α -CuPc film is more conductive (see the lower table). The actual flow current is very important for practical sensor

devices, i. e. the higher the current generated by the sensor is, the simpler a design of the peripheral circuits is. Therefore, we tried to combine the high-conductive film with the high-sensitive film. This attempt was realized by an insertion of the VOPc layer between the α -CuPc single film and the glass substrate. The result is also depicted in Fig. 2. Indeed, the gas sensitivity of the α -CuPc/VOPc film increases, but it gives a non-linear property. The sensitivity of α -CuPc/VOPc film traces that of the VOPc single film upto the gas concentration of 400 ppm. It turns to surpass the property of the VOPc single film beyond 400 ppm. This result suggests a non-linear relationship between the NO₂ adsorption and the conductivity change of α -CuPc /VOPc film. Similar non-linear property has been reported for the amorphous CuPc thin films.²⁾ In order to explain this phenomenon clearly, however, it is necessary to investigate the detailed conduction mechanism of the metal Pc (MPc) films. In spite of this high sensitivity, more conducting current is available for the α -CuPc/VOPc film than that for the VOPc single film probably due to a contribution from the more conductive α -CuPc film, as summarized in the lower table of the figure.

Increase in the gas sensitivity is more pronounced in a low gas concentration range to 1 ppm, as shown in Fig. 3. Insensitivity of the α -CuPc film to the NO₂ gas in this range is drastically improved by the inserted VOPc layer. The typical measured current is listed in the lower table of the figure. Furthermore, the response to 1 ppm NO₂ gas atmosphere for the α -CuPc/VOPc film is reproduc-

Fig. 1 Schematic diagram of the measurement apparatus for the response characteristics to NO₂ gas ambience.

	α -CuPc	VOPc	α -CuPc/VOPc
0ppm	0.85 μ A	0.29 μ A	0.41 μ A
100ppm	2.40 μ A	0.70 μ A	1.20 μ A
1000ppm	12.0 μ A	6.10 μ A	14.0 μ A

Fig. 2 Sensitivity- NO_2 gas concentration characteristics for the α -CuPc and VOPc single films, and the α -CuPc/VOPc film. The measured currents are also listed in the lower table.

	α -CuPc	α -CuPc/VOPc
0 ppm	0.85 (μ A)	0.41 (μ A)
1 ppm	0.85 (μ A)	0.51 (μ A)

Fig. 3 Sensitivity- NO_2 gas concentration characteristics for the α -CuPc single film and the α -CuPc/VOPc film in the low NO_2 gas concentration range to 1 ppm. The lower table shows the measured currents.

ed in cycles of NO_2 doping (for 5 min) and N_2 dedoping (for 10 min) at working temperature of 80°C as shown in Fig. 4, while the recovery characteristics is insufficient. It has been also reported for other metal-phthalocyanine films that the film conductivity does not recover to its initial value resulting in an insufficient reversibility in the response characteristics, in particular, for several

Fig. 4 Time response of the α -CuPc/VOPc film in cycles of 1 ppm NO_2 doping and N_2 dedoping.

cycles of alternated NO_2 doping.⁵⁻⁷⁾ This irreversibility seems to be attributed to an incomplete desorption of NO_2 gas from the film surface. In fact, the sensitivity to same amount of NO_2 gas decreases gradually for the long cycles of alternated gas doping. Heat treatment of the film is necessary to recover the initial film conductivity after the NO_2 gas doping.

It is pointed out in the previous study¹⁰⁾ that the gas sensitivity strongly depends on the film microstructure. Therefore, the above results seem to be closely related to a change of the film microstructure. XRD profiles shown in Fig. 5 reveal that the α -CuPc single film shows a peak at $2\theta = 6.8^\circ$ corresponding to an interplanar distance of $13 \text{ \AA}$, the distance between Cu atoms,¹²⁾ while no peak is detected from the VOPc single film. For the α -CuPc/VOPc film the peak is also completely disappeared, which suggests that a crystal structure of the α -CuPc/VOPc film is influenced by the inserted layer, the VOPc film.

Fig. 5 X-ray diffraction profiles of the α -CuPc and VOPc single films and the α -CuPc/VOPc film. The profile for the glass substrate is also depicted.

Figure 6 shows AFM images of the α -CuPc and VOPc single films and the α -CuPc/VOPc film. All the films are composed of small grains ranging from a few tens of nm to 100 nm in size. Clearly, the grains become large in the α -CuPc/VOPc film which is combined of two kinds of single films. Furthermore, in spite that there is quite difference in the shape and microstructure of grains between the α -CuPc and VOPc single films, the microstructure like a V-shaped grain which is a

Fig. 6 AFM images (500×500 nm in scanning size) of (a) α -CuPc, (b) VOPc and (c) CuPc/VOPc film.

feature of the VOPc film is reflected in the α -CuPc/VOPc film whose overlayer is α -CuPc. Therefore, the drastic improvement of the NO_2 gas sensitivity for the α -CuPc/VOPc film is attributed to the same film microstructure as the higher-sensitive VOPc film. However, the resulting current is associated with the conductivity of the α -CuPc film.

The non-linear property or the relation between the high sensitivity and the V-shaped microstructure still needs further intensive investigations for the α -CuPc/VOPc film. Furthermore, it is very interesting to study on sensing-characteristics of the VOPc/ α -CuPc film. However, the present study clearly shows a possibility to improve the response characteristics of the α -CuPc film-based NO_2 gas sensors through a modification of the film microstructure.

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References

- 1) Y. Sadaoka, N. Yamazoe and T. Seiyama, *Denki Kagaku*, **46**, 597 (1978).
- 2) M. Masui, M. Sasahara, T. Wada and M. Takeuchi, *Applied Surface Science*, **92**, 643 (1996).
- 3) S. Pizzini, G. L. Timo, M. Beghi, N. Butta and C. M. Mari, *Sensors and Actuators*, **17**, 481 (1989).
- 4) C. Hamann, A. Mrwa and M. Müller, *Sensors and Actuators B*, **4**, 73 (1991).
- 5) S. Dogo, J.-P. Germain and A. Pauly, *Thin Solid Films*, **219**, 251 (1992).
- 6) John D. Wright, Philippe Roisin and G. Patricia Rigby, *Sensors and Actuators B*, **13-14**, 276 (1993).
- 7) A. Cole, R. J. McIlroy, S. C. Thorpe, M. J. Cook, J. McMurdo and A. K. Ray, *Sensors and Actuators B*, **13-14**, 416 (1993).
- 8) A. K. Ray, M. J. Cook, S. C. Thorpe and S. Mukhopadhyay, *Phys. Stat. Sol.*, **140**, K 85 (1993).
- 9) A. Chyla, J. Sworakowski, A. Szczurek, E. Brynda and S. Nespurek, *Mol. Cryst. Liq. Cryst.*, **230**, 1 (1993).
- 10) T. Nagasawa, N. Takeuchi, K. Murakami, K. Watanabe, *Bulletin of the Research Institute of Electronics Shizuoka University*, **31**, 99 (in Japanese) (1996).
- 11) C. Gu, L. Sun, T. Zhang, T. Li and M. Hirata, *Thin Solid Films*, **244**, 909 (1994).
- 12) A. W. Snow and W. R. Barger, (Eds., C. C. Leznoff and A. B. P. Lever), *Phthalocyanines properties and applications*, VCH, New York, p. 362 (1989).