Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Improvement in NO_2-Sensing Characteristics of α-Copper Phthalocyanine Thin Films by the Deposition on the Hydrofluoric Acid-Treated Glass Substrates

Tadashi Nagasawa [a], Kenji Murakami [b] & Kenzo Watanabe [a]

[a] Graduate School of Electronic Science and Technology, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432, Japan

[b] Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432, Japan

Version of record first published: 04 Oct 2006

Mol. Cryst. Liq. Cryst., 1998, Vol. 316, pp. 389–392
Reprints available directly from the publisher
Photocopying permitted by license only

Improvement in NO_2-Sensing Characteristics of α-Copper Phthalocyanine Thin Films by the Deposition on the Hydrofluoric Acid-Treated Glass Substrates

TADASHI NAGASAWA, KENJI MURAKAMI*, and KENZO WATANABE*
Graduate School of Electronic Science and Technology, and *Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432, JAPAN

Gas response characteristics of α-form copper phthalocyanine thin film-based NO_2 sensor is drastically improved by a deposition of the film on hydrofluoric acid-treated glass substrate. It is found from the atomic force microscope analyses that this phenomenon is closely related to a modification of the film microstructure.

Keywords: α-form copper phthalocyanine thin film, NO_2 gas sensor, hydrofluoric acid treatment, atomic force microscopy

INTRODUCTION

Although the copper phthalocyanine (CuPc) film-based NO_2 gas sensors have shown high sensitivity[1], their response characteristics are insufficient, in particular, for several cycles of alternated dopings and dedopings[2,3]. There have been several attempts[4-7] to improve the characteristics. It is also known that the structure and morphology of the CuPc thin films strongly influence the gas-sensing characteristics[4,8-11].

In this report, we have attempted to improve the gas response characteristics of the α-form CuPc (α-CuPc) thin films by means of a deposition on a hydrofluoric acid (HF)-treated glass substrate. Analyses by using the atomic force microscope (AFM) were applied to the film microstructures for clarifying the response mechanism.

EXPERIMENTAL

Commercially available α-CuPc (TOKYO KASEI, purity>93%) was used in the present study. It was sublimed at between 450°C and 500°C in the vacuum of 10^{-4} Pa, and deposited at room temperature on glass substrates with and without the HF treatment. The HF treatment was done in a 55% HF solution for one minute. The film thickness was monitored by quartz oscillator to become 200 nm with a deposition rate of 0.1 nm/s.

The 20 finger interdigitated gold electrodes were vacuum evaporated on the α-CuPc film to measure an electric conductivity at a working temperature of 150°C. The conductive current was monitored by using a Keithley 610C electrometer under the dc bias of 10V. The film microstructures were characterized by AFM (JEOL JSTM-4200D) with a non-contact mode in air.

RESULTS AND DISCUSSION

Gas sensitivity of the α-CuPc films deposited on the glass substrates with and without the HF treatment shows a same linear relation in the NO_2 gas concentration range upto 50 ppm. The gas sensitivity is defined as a ratio of the measured current in NO_2 gas to the current in air. The film conductivity itself is higher for the film deposited on the HF-treated substrate than the other. In the NO_2 range higher than 50 ppm, the sensitivity tends to saturate for both films, but that for the film deposited on the HF-treated substrate becomes lower.

Drastic improvement in the gas response reversibility is realized in Fig. 1 for the α-CuPc film deposited on the HF-treated glass substrate. The gas response characteristics were measured in cycles of 50 ppm NO_2 doping and

air dedoping for the films with and without the HF treatment. Usually, the conductivity of the film does not recover to its initial value, and thus the film conductivity continues to increase with the NO_2 doping cycles, as shown in Fig. 1 (closed circles). However, for the film deposited on the HF-treated substrate, the film conductivity recovers completely to its initial value in every cycle. This improvement in the response seems to be attributed to a change of the film properties caused by the HF treatment of the substrate. It has been also pointed out[7] that the gas sensitivity and response characteristics strongly depend on the film microstructure. Therefore, the HF treatment of substrate may be closely related to a modification of the α-CuPc film microstructure.

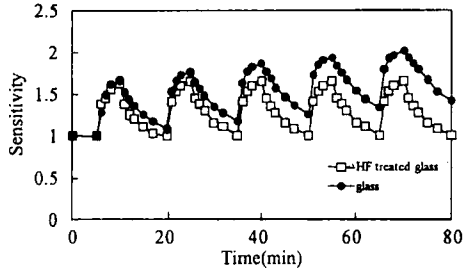

FIGURE 1 Response reversibility in 50 ppm NO_2 doping cycles.

Figure 2 shows AFM micrographs of the α-CuPc films deposited on the glass substrate (Fig. 2(a)), and that on the HF-treated glass substrate (Fig. 2(b)). Although the grain structure can be found in both films, there are some differences in size and shape of the grains. Firstly, the grain size ranges from 20 nm to 100 nm in the film deposited on the glass substrate, while it becomes almost same, about 90 nm, for all grains in the film deposited on the HF-treated glass substrate. Secondly, the film with the HF treatment is more closely packed than the other. As a result, the HF treatment of the substrate causes a homogeneous distribution of almost same sized grains in the film.

Therefore, the improvement in the gas response reversibility of the α-CuPc film deposited on the HF-treated substrate is explained as follows: NO_2 gas molecules are usually adsorbed on the surface and penetrate into the

film because the film deposited on the glass substrate consists of the various sizes of grains leaving many gaps, as shown in Fig. 2(a). However, the grains are closely packed in the film deposited on the HF-treated substrate, and thus, the gases hardly penetrate into the film resulting in adsorbing on and desorbing from only the surface of the film.

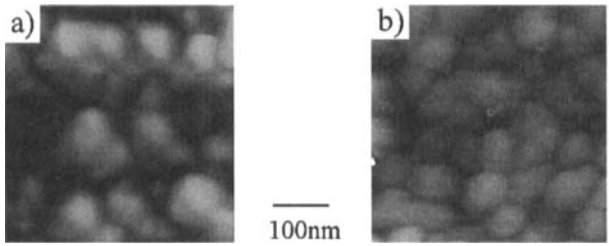

FIGURE 2 AFM micrographs of vacuum sublimed α-CuPc films.

References

[1.] For example: Y. Sadaoka, N. Yamazoe and T. Seiyama, *Denki Kagaku*, **46**, 597 (1978) (in Japanese).

[2.] S. Dogo, J.-P. Germain, C. Maleysson and A. Pauly, *Thin solid films*, **219**, 251 (1992).

[3.] A. Cole, R.J. Mclloy, S.C. Thorpe, M.J. Cook, J. McMurdo and A.K. Ray, *Sensors and Actuators B*, **13-14**, 416 (1993).

[4.] B. Bott and T.A. Jones, *Sensors and Actuators*, **5**, 43 (1984).

[5.] T.A. Jones, B. Bott and S C. Thorpe, *Sensors and Actuators*, **17**, 467 (1989).

[6.] J.D. Wright, P. Roisin and G.P. Rigby, *Sensors and Actuators B*, **13-14**, 276 (1993).

[7.] Y. Sadaoka, M. Matsuguchi, Y. Sakai and Y. Mori, *Sensors and Actuators B*, **4**, 495 (1991).

[8.] S. Pizzini, G.L. Timo, M. Beghi, N. Butta and C.M. Mari, *Sensors and Actuators*, **17**, 481 (1989).

[9.] Y. Sadaoka, M. Matsugachi, Y. Sakai, Y. Mori and W. Gopel, *J. Mater. Sci.*, **25**, 5257 (1990).

[10.] A. Wilson, J.D. Wright and A.V. Chadwick, *Sensors and Actuators B*, **4**, 499 (1991).

[11.] M. Masui, M. Sasahara, T. Wada and M. Takeuchi, *Applied Surface Science*, **92**, 643 (1996).