Electrical Properties and Gas Response in Alternate Layer-by-Layer Films of Copper Phthalocyanine Dyes

Keizo Kato, Naoki Watanabe, Shigenobu Katagiri, Kazunari Shinbo, Futao Kaneko and Rigoberto C. Advincula¹

> Department of Electrical and Electronic Engineering, Niigata University Ikarashi 2-8050, Niigata 950-2181, Japan Phone: +81-25-262-6724, e-mail: keikato@eng.niigata-u.ac.jp ¹Department of Chemistry, University of Houston 136 Fleming Building, Houston, Texas 77204-5003, USA

1. Introduction

Phthalocyanine and porphyrin dyes [1] have been attracting much interest for developing many kinds of electrical and electronic devices. Many studies have been reported for organic solar cells, field effect transistors, organic light emitting diodes, gas sensors, secondary batteries. Certain conducting polymers [2] have achieved limited success in electronic nose applications, and phthalocyanines and porphyrins have attracted interest as organic sensors [3-6]. The electrostatic layer-by-layer (LbL) deposition technique [7] of electrolytes is quite useful for fabricating ultrathin films with nanometer order thickness. This technique can be applied for various kinds of charged materials such as polyelectrolytes, clay, nano-particles and so on. Ultrathin films of phthalocyanine derivatives with proper ionic groupes can also be fabricated using the technique [8].

In this study, alternate LbL films of positively and negatively charged copper phtalocyanine (CuPc) dyes were fabricated and the electrical properties were investigated. The response to NO_2 gas was also examined.

2. Experimental Details

Figure 1 shows the chemical structures of two kinds of CuPc dyes used for the preparation of CuPc alternate LbL films. Alcian Blue, pyridine variant (AB) and copper (II) phthalocyanine-3,4',4",4"'-tetrasulfonic acid, tetrasodium salt (CuPcTs) molecules were positively and negatively charged in the aqueous solutions, respectively, and can be deposited using LbL deposition technique [8]. 3-aminopropyltriethoxysilane (APS) [9], polystyrenesulfonic acid (PSS) and poly (diallyldimethylammonium chloride) (PDADMAC) [10] were also used for fabricating the precursor film which contributes to an excellent deposition of CuPc bilayer films of CuPcTs and AB dyes. Aqueous solutions of the AB and CuPcTs with the concentration of 1mM were prepared for the deposition. The ultrathin films of n bilayers of CuPcTs and AB dyes were fabricated on glass substrates covered with APS monolayer and 1 bilayer of PSS and PDADMAC. CuPc alternate LbL films were deposited by immersion to the aqueous solutions of AB and CuPcTs for 30 min.

Au electrodes were deposited on the CuPc alternate LbL film surface by a vacuum evaporation method in order to measure the electrical properties. The gap between the electrodes was 20 μ m and the electrical properties in the

direction parallel to the surfaces of the CuPc alternate LbL films were measured.



Fig. 1. Chemical structures of AB and CuPcTs dyes used for the preparation of CuPc alternate LbL films.

3. Results and Discussion

The optical absorption spectra of the 1, 3, 5, 10, 20 bilayers of CuPc LbL films on glass substrates were measured and are shown in Fig. 2. The absorption peaks of B and Q bands were observed at around 330 and 620 nm, respectively. The both peaks increase with the number of bilayers. It was found that the alternate LbL deposition of CuPc dyes was successful.

Figure 3 shows the current versus electric field characteristics measured in N_2 and after 15 min exposure to 100 ppm NO_2 gas for the 20-bilayer CuPc LbL film. It was found that the conduction current increased by a thousand times after exposure to 100 ppm NO_2 gas. The plots of the logarithm of the current versus electric field show a linear relationship in the high electric filed region. The properties of the current suggest the hopping conduction of carriers due to Poole effect. The hopping lengths of the carriers estimated from the slopes were about 0.15 μ m in N_2 and 0.44 μ m after exposure to NO_2 gas.



Fig. 2. Absorption spectra of CuPc LbL films with various number of bilayers.



Fig. 3. Current versus electric field characteristics for the 20-bilayer CuPc LbL film in N_2 and after 15 min exposure to 100 ppm NO_2 gas.

The temporal change of the current after exposure to 100 ppm NO₂ gas for the 20-bilayer CuPc LbL film applied at 2 V is shown in Fig. 4. Initially, the response seemed to be fast but the current considerably increased with time and did not saturate even after 30 min exposure to the NO₂ gas. The magnitude of the current after 30 min exposure to the NO₂ gas is about a thousand times as large as that in N₂. This is thought to be because the gas concentration was high. After switching off the NO₂ gas, the current decreased very slowly at room temperature and the recovery time was found to be long.



Fig. 4. Response of the current to 100 ppm NO_2 gas for the 20-bilayer CuPc LbL film applied at 2 V.

4. Conclusions

CuPc alternate LbL films were prepared and the electrical properties were investigated. The mechanism of the electrical conduction was thought to be due to the hopping of carriers due to Poole effect. The response to NO_2 gas was also measured. The conduction current increased by a thousand times after 30 min exposure to 100 ppm NO_2 gas. The response of the current was also measured. The response initially seemed to be fast but the current considerably increased with time and did not saturate even after 30 min. This was thought to be because the gas concentration was high. The results in this work are useful for the development of a highly sensitive gas sensor.

References

- [1] L. R. Milgrom: The Colours of Life (Oxford University Press, Oxford, 1997).
- [2] M. C. Lonergan, E. J. Severin, B. J. Doleman, S. A. Beaber, R. H. Grubb and N. S. Lews: Chem. Mater., 8 (1996) 2298.
- [3] S. Capone, S. Mongelli, R. Rella, P. Sicilano and L. Valli: Langmuir, 15 (1999) 1748.
- [4] T. Richardson, V. C. Smith, R. A. W. Johnstone, A. J. F. N. Sobral and A. M. d'A. Rocha-Gonsalves: Thin Solid Films, 327-329 (1998) 315.
- [5] K. Kato, C. M. Dooling, K. Shinbo, T. H. Richardson, F. Kaneko, R. Treggoning, M. O. Vysotsky and C. A. Hunter: Colloids & Surf. A, 198-200 (2002) 811.
- [6] K. Kato, H. Araki, K. Shinbo, F. Kaneko, C. M. Dooling and T. H. Rivhardson: Jpn. J. Appl. Phys., 41 (2002) 2779.
- [7] G. Decher, J.-D. Hong and J. Schmitt: Thin Solid Films, 210-211 (1992) 831.
- [8] Y. M. Lvov, G. N. Kamau, D-L. Zhou and J. F. Rusling: J. Colloid and Interface Science, 212 (1999) 570.
- [9] K. V. Sarathy, P. J. Thomas, G. U. Kulkarni and C. N. R. Rao: J. Phys. Chem. B, 10 (1999) 399.
- [10] K. Shinbo, M. Minagawa, H. Takasaka, K. Kato, F. Kaneko and T. Kawakami: Colloids & Surf. A, 198-200 (2002) 905.