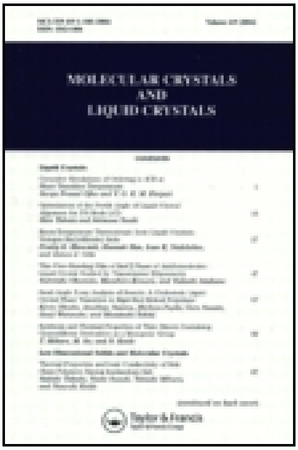

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Fast Gas Sensing with Metal-Phthalocynaine Films in MIS Structures

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The NH_3 gas sensing characteristics of vanadyl-phthalocyanine (VOPc) films in metal-insulator-semiconductor (MIS) heterostructures were investigated. The MIS device showed a rectification behavior and an increase in conductivity at the presence of NH_3 gas. The response was very fast and reversible. The conductivity change observed for the MIS sensors was found to be originating from the change of the barrier height between the junctions.

Keywords: metal phthalocyanine, gas sensor, MIS structure

INTRODUCTION

The conductivities of metal phthalocyanines (MPc) are easily modified by the presence of gases, which leads to a considerable interest in their practical use as gas sensors [1]. Most MPc compounds are known to show *p*-type semiconducting behavior [1, 2]. Their conductivities increase at the presence of electron acceptor gases such as O_2 and NO_x, and decrease with electron donor gases such as ammonia. These experimental results are explained by the change of the hole concentration in the MPc (*p*-type semiconductor) films. Gas sensing devices fabricated so far were mostly in the form of thin film chemiresistors prepared by the thermal evaporation of MPc compounds and metal electrodes onto insulating substrates. Various efforts have been done to improve the sensitivity, reversibility, and selectivity of the sensors.

In the present study, we investigated NH_3 gas sensing properties of VOPc films in the form of metal-insulator-semiconductor (MIS) structure. We used gold and VOPc films as the metal electrode and the insulating layer, respectively. Since the resistivity of VOPc films are rather high, VOPc layers can be regarded as insulators in the heterostructures fabricated. The n-type Si (111) surfaces whose dangling bonds were terminated with hydrogen atoms by HF etching were used as the substrates. Gold electrodes on n-type Si show Schottky junction behavior.

It has been reported that gas sensor devices having Schottky junctions such as Pd/CdS [3], Pt/TiO_2 [4] and Pd/Si [5] can detect H_2 gas due to the change in the work function of metals with H_2 occlusion. Thus it seems feasible to detect various gases by inserting the suitable organic layers between metals and semiconductors. In addition, chemical sensors with MIS structures have advantages in ease of nano-fabrication.

EXPERIMENTAL

VOPc powder purchased from Kanto Chemical Ltd.was purified by vacuum sublimation before use. Hydrogen-terminated *n*-type Si(111) substrates were prepared using HF and NH_4F solutions according to the method reported previously [6]. The substrate was introduced in a vacuum chamber immediately after the treatment. VOPc film growth was carried out in the chamber with a base pressure of 2×10^{-5} Pa. The substrate was kept at room temperature during film growth. The thickness and growth rate of the films were about 40 nm and 0.3 nm /min, respectively, which were measured with a quartz oscillator located near the substrate. Gold electrodes with a thickness of 30 nm were subsequently evaporated on the VOPc films.

The dark conductivity of the specimens was measured in a vessel in which the atmosphere could be controlled. Indium-gallium alloy was used as the conducting paste for ohmic contacts on the n-type Si substrate. The NH_3 gas was diluted with zero-grade air to required concentration in the range from 100 to 1000 ppm (by volume).

Gas sensing properties of VOPc films evaporated on a glass plate which was fitted with gold interdigital electrodes were also investigated. The electrode consisted of 32 finger pairs with a thickness of 30 nm and an inter-spacing of 100 μm.

RESULTS AND DISCUSSION

Figure 1 shows the dark current-voltage (I-V) characteristics of VOPc films grown on a glass substrate. The solid and dashed curves are the results measured in the air and NH_3 (1000 ppm) atmosphere, respectively. The current response is linear over the range of applied bias voltage, indicating good ohmic contacts between the gold electrode and the VOPc film. The presence of NH_3 causes a decrease in dark conductivity. This can be understood by considering that VOPc is a p-type semiconductor and NH_3 acts as an electron donor in the film. Chemisorbed NH_3 molecules decrease the hole concentration in the VOPc film, resulting in a decrease of conductivity.

Figure 2 shows the I-V characteristics of the MIS cell in the air and NH_3 (1000 ppm) atmosphere. The cell shows the rectification behavior originating from the difference in the work function between silicon and gold. The conductivity increases in the NH_3 atmosphere at both positive and negative bias voltages, which is different from the results shown in Fig. 1. Thus the conductivity change of MIS structures observed in the present experiment is not explained by the doping effect of electron donors in the VOPc films.

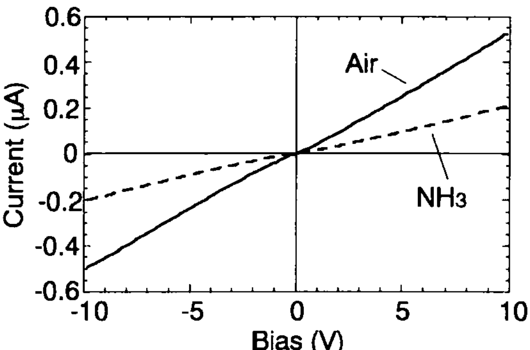

FIGURE 1. I-V characteristics of VOPc films grown on glass in the air (solid curve) and NH_3 (1000 ppm) atmosphere (dashed curve).

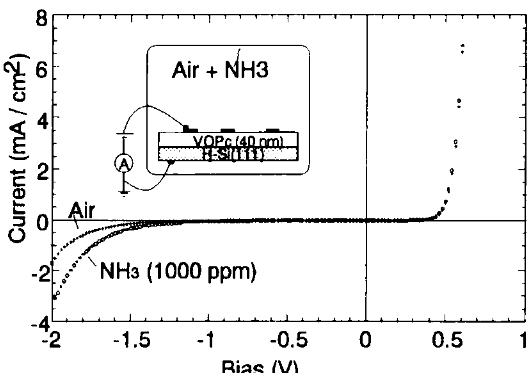

FIGURE 2. I-V characteristics of VOPc films in the MIS form measured in the air (crosses) and NH_3 (1000 ppm) atmosphere (open circles).

Figure 3 shows the response of the MIS cell to the NH_3 (200 ppm) gas at the bias voltage of -1.0 V. The sensitivity is represented by the relative conductivity change $(\sigma_0-\sigma_t)/\sigma_0$, where σ_0 is the initial conductivity of the cell before exposure to NH_3 gas, and σ_t is the conductivity after exposure for time t. It changes by more than 30 % within 3 sec after exposure to the NH_3 gas. The conductivity decreases to the initial value rapidly in the air atmosphere. This suggests that the NH_3 molecules adsorbed on the surface govern the sensing property of MIS structures. NH_3 molecules adsorbed on the surface modify the barrier height of the MIS structure and result in the fast conductivity change.

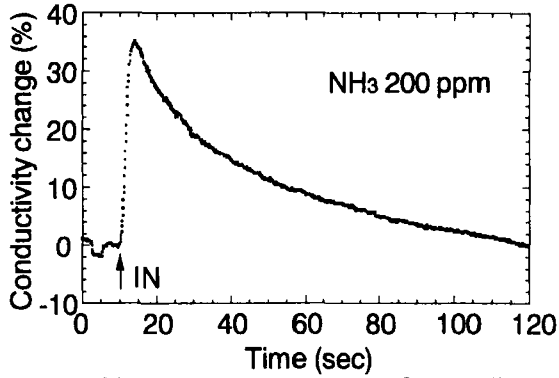

FIGURE 3. Response curve of MIS cell to NH_3 (200 ppm) gas.

In summary, new type gas sensors were fabricated with phthalocyanine films in the form of MIS structures. The conductivity change by adsorption of NH_3 molecules was thought to originate from the change of the barrier height. Chemical sensors with MIS structures using organic films have potentials in sensitivity, reversibility, responsibility, and selectivity, and in ease of nano-fabrication.

Acknowledgments
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