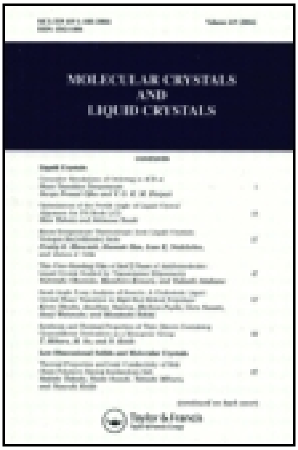

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NO_2 Gas Sensing with Au/Phthalocyanine/Si Heterostructures

Hirokazu Tada [a], Yasuaki Tanimura [a], Yasuhiro Fujii [a] & Kazumi Matsushige [a]

[a] Department of Electronic Science and Engineering, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto, 606-8501, Japan

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NO_2 Gas Sensing with Au / Phthalocyanine / Si Heterostructures

HIROKAZU TADA, YASUAKI TANIMURA, YASUHIRO FUJII and KAZUMI MATSUSHIGE

Department of Electronic Science and Engineering, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606–8501, Japan

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The current-voltage characteristics of the heterostructure cell of Au / vanadylphthalocyanine (VOPc) layers/ Si were investigated in NO_2 atmosphere. The cells showed a rectification behavior and an increase in current at the presence of NO_2 gas. The NO_2 gas was detected even for the Au/Si cell without VOPc layers and the sensitivity was found to be enhanced significantly by insertion of VOPc layers. The cell with 10 nm-thick VOPc layers exhibited an increase in current density by a factor of 15 in 6 ppm NO_2 atmospher It was thus suggested that the interface between Au/Si and VOPc/Si play a key role to determine the gas sensing properties. The adsorbed NO_2 gas molecules are thought to modify the interface potential.

Keywords: metal phthalocyanine; gas sensor; interface potential

INTRODUCTION

Chemical sensors for quantitative detection of toxic gas become the important object of the next century. Various methods have been investigated and some of them are put to practical use. Among them, the sensors based on the modification of interface potential due to gas adsorption have become of interest in recent years. Schottky diodes [1-3] and metal-oxide-semiconductor field-effect-transistors (MOSFETs) [4, 5] are designed to detect hydrogen gas. The sensitivity for hydrogen gas is attributed to the modification of the work function of the metal gate electrode due to the gas adsorption. Catalytic metals such as Pd and Pt employed as gate electrodes play key roles in the sensing.

In the previous paper, we demonstrated the ammonia gas detection at the interfaces in the heterostructures, gold electrode/phthalocyanine films/silicon [6], where it was suggested that the interface potential was modified by the adsorbed ammonia gas in phthalocyanine films. An additional advantage in this sensor is to employ organic thin layers as adsorbent. If appropriate organic materials are chosen, an effective detection of the specific gas molecules can be acieved. In order to improve the selectivity and sensitivity, however, the systematic investigation with various conditions are now required. In the present study, we investigated NO_2 gas sensing properties of the heterostructures. The NO_2 gas is known to be a powerful oxidizing agent. The effect of NO_2 gas exposure on chemical and electronic structure of the heterojunctions will be discussed.

EXPERIMENTAL

Two types of the substrates were prepared by chemical treatment of n-type Si(111) wafers (1 Ωcm). One was hydrogen-terminated Si(111) surface prepared using HF and NH_4F solutions. Another one had the chemically oxidized thin layer on the surface by boiling the H-Si(111) in the mixture solution of HCl and H_2O_2. The substrates thus prepared were introduced immediately into a vacuum chamber. Vanadyl-phthalocyanine (VOPc) powder (Kanto Chemical Ltd.) was purified by vacuum sublimation and charged in a quartz crucible of a Knudsen-cell. 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 growth rate of the films was controlled to be about 0.3 nm /min with a quartz oscillator located near the substrate. The VOPc layers with various thickness in the range from 3 nm to 50 nm were prepared on the substrates. Gold electrodes with a thickness of 30 nm were subsequently evaporated on the VOPc films.

The dark conductivity of the specimens was measured in another vacuum chamber with a volume of 3 *l* in which the atmosphere could be controlled. The standard gas of NO_2/N_2 (100 ppm, Nippon Sanso) was diluted at an appropriate concentration with pure N_2 gas (99.999%, Nippon Sanso) using a mass flow controlled gas blender (Stec, SECB-2), and was introduced into the measurement chamber with a ratio of 1 *l* /min.

Indium-gallium alloy was used as the conducting paste for ohmic contacts on the n-type Si substrate. The cells show the rectification behavior in current-voltage measurement originating from the Au/Si heterojunction. The sensitivity is represented by the relative current density ρ_{gas}/ρ_0, where ρ_0 is the initial current density of the cell before exposure to NO_2 gas and ρ_{gas} is the saturated current density in NO_2 gas atmosphere. The sensitivity at the reverse bias voltage was found to be higher than that measured at forward bias voltage. Thus the response behavior to the gas was measured at the reverse bias voltage of 5 V.

RESULTS AND DISCUSSION

Figure 1 shows the response curves of the Au/H-Si cell to NO_2 (98 ppm) gas. The gas inlet valve of the chamber was opened at time 0 and then closed after three minutes to fill the chamber with the NO_2 gas of atmospheric pressure. After each measurement, the chamber was pumped out until the current became stable. It should be noted that the cell even without VOPc layer responded clearly to the NO_2 gas. The current increased rapidly by a factor of 3 from the initial value at the first time exposure to the freshly prepared cell and then it decreased gradually. The response curves for the second and third time exposure show gradual increase to the saturated values. The unique response observed for the freshly prepared cell is possibly due to the oxidization of the silicon surface through the reaction with NO_2 molecules, since the cells with thick oxide layers on silicon exhibited gradual increase in current to the saturated value like the curves (b) and (c) in Fig. 1. The sensitivity increased with the number of measurement. Thus the oxidized surface seems to play an important role in the gas detection behavior.

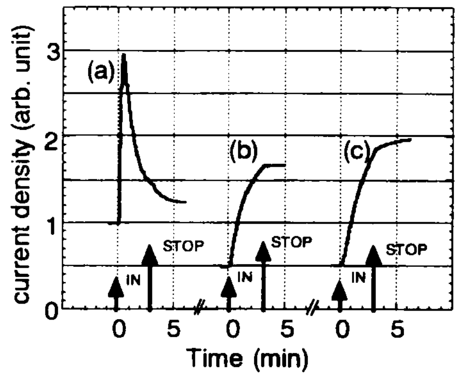

FIGURE 1. Response curves of Au/H-Si cell to NO_2 (98 ppm) gas at the 1st time exposure to the freshly prepared cell (a), 2nd time exposure (b), and 3rd time exposure (c).

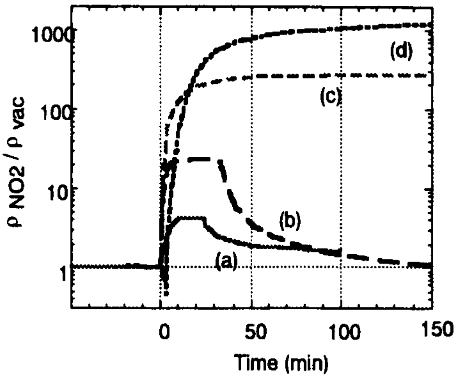

FIGURE 2. Response curves of the cell with variou VOPc layer thickness to NO_2 (98 ppm) gas: (a) VOPc 0 nm, (b) 3 nm, (c) 10 nm, and (d) 50 nm.

Figure 2 shows the response curves of the Au/VOPc/chemically oxidized silicon with various VOPc layer thicknesses measured at the presence of NO_2 (98 ppm) gas. The gas was introduced into the chamber at time 0 for each cell. The current through Au/Si junctions increases by a factor of 4 at the presence of NO_2 gas as shown in curve (a). The curves (a) and (b) exhibit a decrease in current. This is possibly due to the oxidization of the surface as mentioned above. The thick VOPc layers are found to prevent the surface from the reaction as shown in curves (c) and (d). The sensitivity increased with the thickness of VOPc layer, although the response became slow. The sensitivity of the cell with 50 nm-thick VOPc layer is about 1000. The details for such significant enhancement in the gas sensitivity have not elucidated yet, but it is suggested that the adsorbed NO_2 gas molecules modify interface potential which results in the increase in conductivity.

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