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Two types of moisture effects on the receptor function of neat tin oxide gas sensor to oxygen

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ABSTRACT

Influences of moisture on the response of a neat tin oxide gas sensor to oxygen at 623 K were investigated. Two types of moisture effects were easily recognized, that is, moisture acted as a inhibitor to the oxygen adsorption in form of O^- (type I sites) and O^{2-} (type II sites) by being adsorbed competitively (short term effect), whereas the moisture admitted at elevated temperature acted as a promoter to increase the population of type II sites or the adsorptive strength of type I sites (long term effect). A tremendous increase of the type II site population as well as the existence of threshold pressure for oxygen adsorption on the same sites suggests the formation of a sort of surface hydrate, dehydration of which seems to leave type II sites behind. The response to oxygen could be reproduced satisfactorily by using adsorption constants of oxygen and water, threshold pressure of oxygen and semiconductor properties of tin oxide.

1. Introduction

Oxide semiconductor gas sensors, first proposed by Seiyama et al. [1] and Taguchi [2] in 1962, are fabricated with tiny crystals of an n-type metal oxide such as SnO_2. Endowed with excellent sensitivity to oxidizing or reducing gases, beside other advantageous properties such as low cost and long term stability, the sensors of this group have been put in market as gas alarms world-wide. With the concerns to environments and quality of life ever increasing recently, it is highly expected to apply those for monitoring dilute gases indoor or outdoor. However, there is a gap between gas alarms and gas monitors. Gas alarms, aiming at protecting people from fatal gas accidents, are required to detect securely a target gas in problem well before its concentration reaches a fatal level. Gas monitors, on the other hand, is required to monitor a selected gas as precisely as possible. This requirement has been rather hard to be met by a semiconductor sensor because its resistance in air (base resistance) tends to suffer from drifting more or less depending on the humidity surrounding it or having surrounded it. In this regard, moisture has been known as one of the most typical disturbing gases to the sensors. It is well know that on increasing humidity in ambient air the base resistance is reduced significantly, accompanied by a loss in the response to a target gas [3]. This is a moisture effect appearing instantly (short term effect). To a further complication, it has been recognized by experts concerned that high humidity in summer tends to cause the base resistance to shift up to a level so called summer resistance, while low humidity in winter tends to cause an opposite effect (winter resistance) [4]. This is a moisture effect appearing in a long term as the cycle of the seasons (long term effect). Evidently, in order to improve the precision of gas monitoring, one has to either eliminate these moisture effects effectively or find a way to calibrate them. Various attempts have been made empirically to mitigate the moisture effects almost in vain, because there has been a lack of a theoretical base on which the moisture effects are revealed and discussed from a basic standpoint.

Some years ago we succeeded in deriving a theory to describe how oxide semiconductor crystals respond to a change in gas ambient (receptor function) [5–8] and how the gas reception of individual crystals is transduced into a change in device resistance (transducer function) [9]. Based on the theory, the dependence of device resistance on the partial pressure of oxygen (P_{O_2}) was shown to be well accounted for by assuming oxygen adsorption in form of O^- ions [5,8]. The response to a reducing gas (H_2) or an oxidizing gas (NO_2) in air could also be accounted for well [6,10]. Recently, however, we found that oxygen adsorption depends very much on the humidity in gas ambient. That is, in the ambient desiccated to extraordinarily low humidity (0.01% H_2O or less), oxygen adsorption in form of O^{2-} dominates over that in O^-, while in the ambient containing the humidity of 0.1% H_2O and above the formation of O^{2-} ions is suppressed almost completely to be replaced by only O^- ions. Thus the receptor function has been extended to include

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the formation of O^{2-} ions [11]. At the same time, we found that the amounts of formation of O^{2-} and O^{-} ions were strongly influenced by the humidity adopted in the pretreatment of the device. Obviously, this phenomenon is relevant to the long term effect of moisture observed in practice, to be contrasted with the short term effect mentioned above.

From such recognition, we tried to investigate the two types of humidity effects from a basic standpoint. A neat tin oxide device was pretreated in various humidified ambient at elevated temperature to measure its response to oxygen at 623 K in variously humidified ambient. The response was analyzed as a function of coexistent humidity to reveal the nature of the competitive adsorption of oxygen and water on two types of adsorption sites (short term effect of moisture). The analysis was then extended to include the influences of the pretreatment humidity to reveal the nature of the long term effect of moisture. This paper aims at reporting the results of these investigations.

2. Typical phenomena relevant to moisture

All of the following experiments were carried out with a single, neat SnO_2 thick film device (30 μm thick, consisting of SnO_2 grains of 6 nm in radius), which was screen-printed on an alumina substrate attached with comb-type electrodes. Prior to each measurement at 623 K, the device was subjected to a pretreatment, which consisted of heating at 853 K for 2 h in the oxygen gas humidified to the water vapor pressure of 0–0.04 atm, and then cooling in the same gas ambient at a rate of 1 K min^{-1} down to 623 K. The partial pressure of water vapor applied for the pretreatment is expressed as $P_W(P)$ hereafter. The partial pressure of oxygen or water vapor, P_{O_2} or P_W, was varied at 623 K to measure their influences on the electric resistance of the device. All measurements were performed in a gas flow apparatus (100 cm^3 min^{-1}) at a total pressure of 1 atm, while P_{O_2} and P_W were adjusted by controlling the flow rates of nitrogen and oxygen, dried or humidified, as reported elsewhere [12]. It is worth being commented that, although the response of the device changed drastically with a change in P_W and $P_W(P)$, the changes were quite reversible; exactly the same response could be attained under the same conditions of P_W and $P_W(P)$. This assures that all of the moisture effects observed here are reversible, free from any irreversible changes of SnO_2 grains.

For theoretical analysis, device resistance (R) should be converted into response, $x = R/R_0$, where R_0 is the resistance at flat band state. Fortunately, R_0 has been found to be very close to the resistance in humidified nitrogen gas (R_{N_2}). In the present study, R/R_{N_2} was used as the response to oxygen whenever R_{N_2} was measured. Otherwise 500 Ω was allotted to R_{N_2} as an approximation, since the measured values of R_{N_2} for the particular device used here fell in a narrow range between 450 and 550 Ω, slightly decreasing with increasing P_W of the nitrogen atmosphere. The response obtained in this way will be expressed as R/500.

2.1. Influences of P_W (short term effect)

As mentioned above, domination of O^{2-} and O^{-} ions has been confirmed in the absence and presence of humidity, respectively. With increasing partial pressure of oxygen (P_{O_2}) in desiccated conditions, device response (R/500) grew roughly in proportion to $(P_{O_2})^{1/4}$ to attain large values, as shown in Fig. 1, where P_W and $P_W(P)$ were set to be small as shown. Such response behavior was typical to the formation of O^{2-} ions. Under non-desiccated conditions, on the other hand, R/R_{N_2} increased roughly in proportion to $(P_{O_2})^{1/2}$, typical to the O^{-} formation, as shown in Fig. 2, where P_W

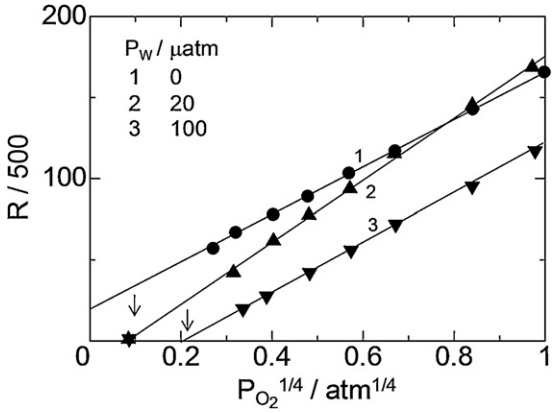

Fig. 1. Response of SnO_2 device (R/500) to oxygen in drier ambient as correlated with $P_{O_2}{}^{1/4}$. Pretreatment humidity ($P_W(P)$) was the same as the measuring humidity P_W shown. Arrows indicate thresholds for the response.

was changed with $P_W(P)$ kept unchanged. Details of the response behavior will be described later. The drastic change of response from that in the desiccated conditions indicates that the O^{2-} formation has been poisoned almost completely in the presence of moisture. In addition, the proportionality constant (slope) is seen to decrease with increasing P_W, indicating that the O^{-} formation is also poisoned significantly by moisture. A comment is added here regarding the non-ideal behavior of line 1 in Fig. 1. Ideally the line is expected to intersect ordinate at $R/R_{N_2} = 1$, while the experimental extrapolation is seen to deviate significantly from the ideal. This deviation is considered to have arisen because the steady values of R could be measured precisely enough due to a kinetic reason, as discussed previously [11]. The relevant measurements were carried out by lowering P_{O_2} stepwise from 1 atm. The rate of desorption of O^{2-} ions was made increasingly smaller as P_{O_2} was lowered. This trend was made far more conspicuous in the absence of humidity (dry condition); it took one day or more for R to reach steady state in the smaller region of P_{O_2} under dry condition.

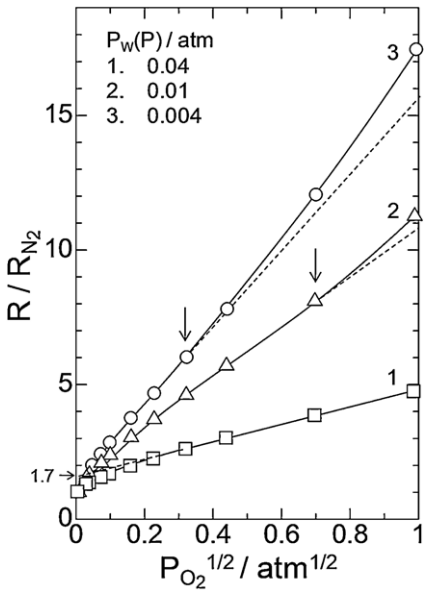

Fig. 2. Response of SnO_2 device (R/R_{N_2}) to oxygen in wetter ambient as correlated with $P_{O_2}{}^{1/2}$ (pretreatment humidity $P_W(P) = 0.04$ atm). Arrows indicate the points deviation from linearity starts at.