

Sensitive and Selective Ammonia Gas Sensor Based on Molecularly Modified SnO₂[†]

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† Presented at the EuroSensors 2017 Conference, Paris, France, 3–6 September 2017.

Published: 25 August 2017

Abstract: The development of selective and cheap metal oxide gas sensor at ambient temperature is still a challenging idea. In this study, SnO₂ surface functionalization was performed in order to obtain sensitive and selective gas sensor operated at ambient temperature. 3-aminopropyltriethoxysilane (APTES) was used as an intermediate step, followed by functionalization with molecules having acyl chloride with different end functional groups molecules such as alkyl, acid and ester groups. Acid and ester modified sensors are sensitive to ammonia between 0.2 and 10 ppm at room temperature. However, ester modified SnO₂ is more selective than acid modified sensor regarding ethanol and carbon monoxide gases.

Keywords: SnO₂; molecular modification; APTES; gas sensor; sensitivity; selectivity; ammonia; ambient temperature

1. Introduction

A simple and noninvasive tool for disease diagnosis is offered by the detection of gases in exhaled breath. Metal oxide chemical sensors are promising devices because they are small, easy to use and less expensive than other spectrometry techniques [1]. For such application, the gas sensor should be sensitive to low concentration of gas and selective to one gas in presence of other gases. Tin dioxide material allows the detection of many gaseous compounds. Nevertheless, the SnO₂-based sensors suffer from two major drawbacks which constitute an obstacle to their development. SnO₂ has lack of selectivity because it has high affinity with many gases. In addition, SnO₂ has high operating temperature between 250 °C and 500 °C. One way to cover these drawbacks is the surface molecular functionalization of SnO₂. Some work on silicon nanowire field effect transistors showed change in the working principle of the sensor. In this case, the interactions are between the gas and the grafted organic layer rather than the metal oxide substrate. The interactions of gases with the attached layer lead to change in the dipole moment that variate the electrical properties of substrate (e.g., SnO₂) [2]. Such modified sensors work at ambient temperature which reduces the power consumption since these sensors will be used in portable devices.

In this work we are intended to achieve surface functionalization of SnO₂ thick film. The functionalization of SnO₂ was performed to cover these well-known disadvantages. The purpose of functionalization was to passivate the surface states on the SnO₂ sensors by molecular layer aiming to optimize their interactions with ammonia gas. The first step of molecular modification is the attachment of APTES. The second step is to fix alkyl, acid and ester functional

groups on APTES modified SnO₂. These sensors are tested to ammonia gas at room temperature. The selectivity is examined versus ethanol, carbon monoxide and acetone gases.

2. Materials and Methods

In this study, SnO₂ thick films are deposited on alumina substrate by screen-printing technique. A semi-automatic Aurel C890 machine was used. The procedures for preparing the SnO₂ ink and sensor fabrication parameters have been described elsewhere [3]. The SnO₂ ink is produced by mixing SnO₂ powder (Prolabo Company) with a solvent and an organic binder. This ink was then screen printed on an alpha-alumina substrate (38 × 5 × 0.4 mm³) provided with sputtered gold electrodes. The deposited SnO₂ material is finally annealed for 10 h at 700 °C in air to get SnO₂ film with a thickness of 40 microns. The SnO₂ particles sizes of the elaborated films were found to be around 75 nm.

The functionalization of SnO₂ was carried out by two steps which lead to covalent attachment of alkyl, acid and ester end functional groups. The first step is the condensation reaction between the hydroxyl groups present on SnO₂ surface and 3-aminopropyltriethoxysilane (APTES from ACROS Organics). This step generates a film terminated by amine groups (SnO₂-APTES) which will act as a substrate for the second step of modifications. Silanization in liquid phase has been described elsewhere [4]. In a first step, SnO₂ sensors were immersed in 50 mM APTES dissolved in 95% absolute ethanol and 5% of deionized water for 5 h under stirring at room temperature. After reaction, the sensors were rinsed with absolute ethanol and dried under N₂ flow to remove the unbounded APTES molecules. As a second step, these terminal amine groups of APTES allow the coupling reaction with molecules bearing acyl chloride group. In the second step, alkyl, acid and ester end group grafting was achieved by immersing APTES modified SnO₂ in a solution of 10 mM of hexanoyl chloride (98%, ALDRICH, alkyl: C₆H₁₁ClO), 1,4-butanedicarbonyl chloride (98%, Fluka, acid: C₆H₈Cl₂O₂) or methyl adipoyl chloride (96%, Alfa Aesar, ester: C₇H₁₁ClO₃), with 5 µL of triethylamine (Fluka) in 5 mL of chloroform as solvent for 12 h under stirring. The sensors were then rinsed with chloroform and dried under N₂ flow.

The elaborated sensors were tested under gases in a test bench at 25 °C to check the effects of functionalization on sensor performance. In this test bench, sensors are installed in an 80 cm³ glass chamber under constant gas flow of 15 L/h. It is provided with gas mass flow controllers which allow controlling the concentrations of different gases at same time. The sensitivity was tested to ammonia gas at 25 °C with air containing 5% of relative humidity (RH). It is defined as the slope of the tangent on the curve of response ($G_N - G_A / G_A$, with G_N : conductance after 20 min of ammonia injection, and G_A : conductance under air with 5%RH) versus ammonia concentration. Sensors selectivity was tested versus ethanol, carbon monoxide and acetone gases.

3. Results and Discussion

The first part of the test under gases was to show the characteristic of the response of different sensors to ammonia gas. As shown in Figure 1, the sensors were tested to 100 ppm of ammonia balanced with 5%RH air at 25 °C. The conductance of pure SnO₂ decreases upon exposure to ammonia gas. This type of response has been founded before by Kamalpreet Khun Khun et al. [5] at temperature between 25 to 200 °C. SnO₂-APTES shows no change in conductance upon exposure to ammonia. This implies that no significant interactions occur between the grafted APTES and ammonia gas. In term of polarity and other chemical properties like acidity, the amine and ammonia groups are almost the same, since amine is one of the derivatives of ammonia. Hence, such response was expected for SnO₂-APTES. In addition, this behavior indicates that the SnO₂ surface is well covered by APTES molecules because the negative response observed on pure SnO₂ is totally inhibited.

SnO₂-APTES-ester, SnO₂-APTES-acid and SnO₂-APTES-alkyl exhibit increase in conductance upon exposure to 100 ppm of ammonia gas (Figure 1). However, the response of SnO₂-APTES-ester and SnO₂-APTES-acid are more important than that of SnO₂-APTES-alkyl. These responses could be related to the different polarities of the attached end functional groups. The interaction of ammonia with ester and acid modified SnO₂ is dipole-dipole while it's induced-dipole in the case of alkyl

modified sensor. In addition, dipole-dipole interaction is always stronger than induced dipole interaction [2]. These interactions of ammonia molecule with the attached end functional groups lead to variation in the dipole moment of the molecular layer. The variation in the molecular layer's dipole moment affects the electron mobility in SnO_2 film which modifies the conductance [6].

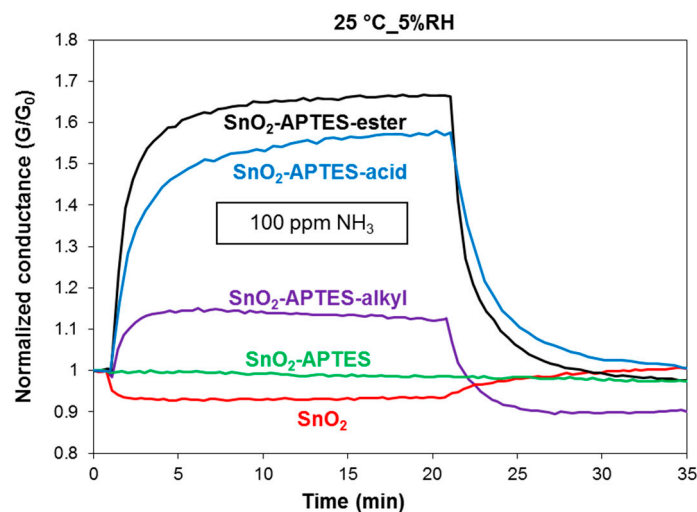


Figure 1. The sensor response of SnO_2 , SnO_2 -APTES, SnO_2 -APTES-alkyl, SnO_2 -APTES-acid and SnO_2 -APTES-ester to 100 ppm of ammonia gas balanced with humid air (5%RH) at 25 °C. G is the conductance at any time and G_0 is the conductance at the beginning of the test ($t = 0$).

Regarding the different sensors sensitivity against ammonia concentrations, Figure 2 shows the relative responses versus ammonia concentrations of SnO_2 -APTES-ester and SnO_2 -APTES-acid in comparison with pure SnO_2 , SnO_2 -APTES and SnO_2 -APTES-alkyl sensors. Pure SnO_2 and SnO_2 -APTES sensors have almost no sensitivity to different ammonia concentrations. In addition, SnO_2 -APTES-alkyl gives no significant response between 0.2 ppm and 30 ppm. It can be noticed that SnO_2 -APTES-ester and SnO_2 -APTES-acid exhibit constant sensitivity between 0.2 ppm and 10 ppm, around 0.023 ppm^{-1} .

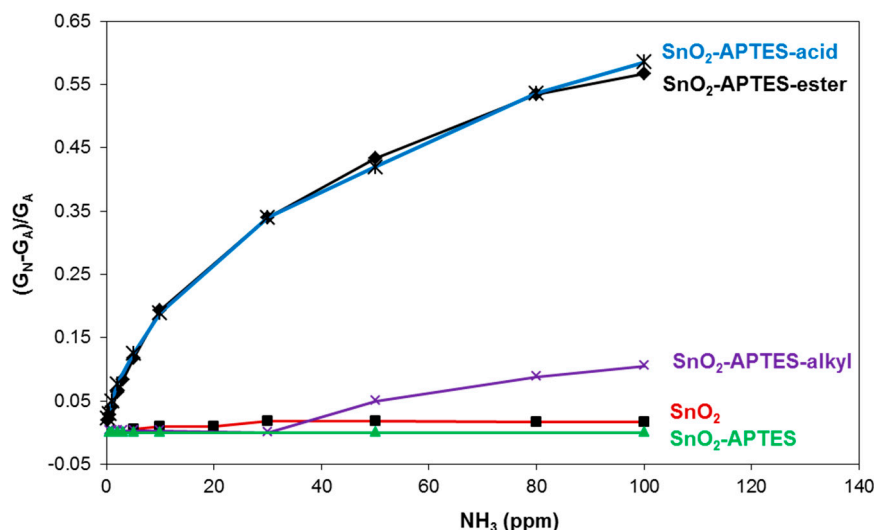


Figure 2. Relative response of SnO_2 , SnO_2 -APTES, SnO_2 -APTES-alkyl, SnO_2 -APTES-acid and SnO_2 -APTES-ester sensors versus ammonia concentrations in 5%RH air at 25 °C.

Concerning the selectivity of ester and acid modified sensors, Figure 3 shows that the SnO_2 -APTES-ester sensor has almost no change in conductance upon exposure to 50 ppm of ethanol, carbon monoxide and acetone at 25 °C. This means that ester modified sensor is selective to

ammonia, at least in regards of the three tested gases. However, acid modified SnO₂ shows less selectivity than ester modified sensor versus ethanol and carbon monoxide. This particular selectivity derives from the unique interactions of the grafted layer on SnO₂ with ammonia gas.

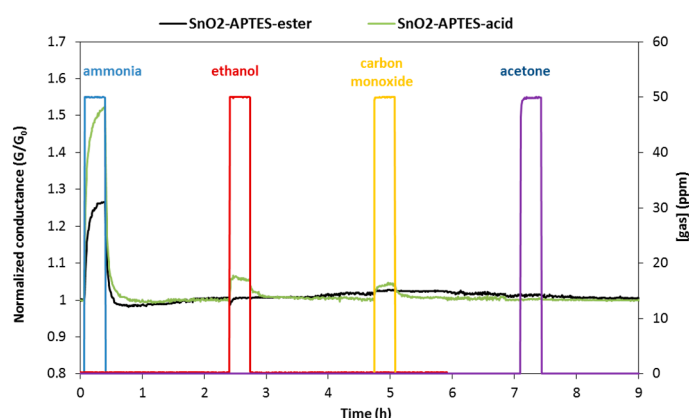


Figure 3. The sensor response of SnO₂-APTES-ester and SnO₂-APTES-acid upon exposure to 50 ppm of ammonia, ethanol, carbon monoxide and acetone gases in humid air (5%RH) at 25 °C.

4. Conclusions

SnO₂ thick films were produced by screen printing and molecularly modified by solution chemical processes. Pure SnO₂ sensor and APTES modified SnO₂ didn't show any significant sensitivity to ammonia between 0.5–100 ppm under 5%RH at 25 °C. On the contrary, ester and acid modified sensors show constant sensitivity between 0.5 and 10 ppm to ammonia (0.023 ppm⁻¹) at 25 °C. Moreover, ester modified SnO₂-APTES sensor is more selective to ammonia gas with respect to reducing gases like ethanol, carbon monoxide and acetone than the acid modified one. As a conclusion, ester modified sensor is a good candidate for breath analysis applications for the diagnosis of diseases related to ammonia gas biomarker. Furthermore, working at ambient temperature is an important challenge to fulfill in view of flexible sensing substrate. Here, a potential molecular modification of SnO₂ for smart devices and portable applications has been put in evidence by our results.

Conflicts of Interest: The authors declare no conflict of interest.

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