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Modified SnO₂-APTES gas sensor for selective ammonia detection at room temperature

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Abstract

The feasibility of room temperature ammonia gas sensors based on tin dioxide (SnO₂) functionalization has been demonstrated. 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. Modified films were characterized by attenuated total reflectance infra-red spectroscopy (ATR-FTIR). Upon exposure to ammonia gas, the electrical conductance of alkyl, acid and ester modified SnO₂-APTES increases, whereas other reducing gases such as ethanol, carbon monoxide and acetone show no change in conductance. Furthermore, ester modified SnO₂ is more selective than acid modified sensor regarding ethanol and carbon monoxide gases.

Keywords: SnO₂; Screen printing; Molecularly functionalization; APTES; Gas sensors; Ammonia gas; Selectivity; Room temperature detection

1. Introduction

The detection of ammonia gas is of great interest in many fields such as medical and environmental monitoring. Ammonia can be detected by different sensing materials like carbon nanotubes or polyaniline [1]. Metal oxide gas sensors are promising devices because they are small in size, easy to use and less expensive than other spectrometry techniques. Thick films of metal oxide can be produced by screen printing which is simple, reproducible and low cost technique. 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. Many approaches were described in the literature to cover these drawbacks e.g. SnO₂/carbon nanotubes and SnO₂/polyaniline hybrid sensors. Another way is the surface molecular functionalization of SnO₂ [2]. Functionalization on silicon nanowire field effect transistors has showed changes in the working principle of the sensors, while these sensors are still lack to selectivity. In this case, the interactions are between the gas and the grafted organic layer rather than the metal oxide substrate. These interactions lead to changes in the dipole moment that variate the electrical properties of substrate (e.g. Si) [3]. Molecular modified SnO₂ sensors work at ambient temperature for selective ammonia detection is not reported in literature. This sensors has low power consumption, hence it can be used in smart portable devices.

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In this work, we were intended to achieve surface functionalization of SnO₂ thick film. 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 was the attachment of APTES. The second step was to fix alkyl, acid and ester functional groups on APTES modified SnO₂. These sensors were tested to ammonia gas at room temperature. The selectivity was examined versus ethanol, carbon monoxide and acetone gases.

2. Experimental section

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 [4]. 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 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 modification. Silanization in liquid phase has been described elsewhere [5]. 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. 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 hours under stirring. The sensors were then rinsed with chloroform and dried under N₂ flow.

The obtained 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, sensor is 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. Sensors selectivity was tested versus ethanol, carbon monoxide and acetone gases.

3. Results and discussion

Regarding the characterization of the functionalized films by ATR-FTIR, the most important signals corresponding to APTES were found between 800 and 1800 cm⁻¹ as shown in Fig. 1. The peak at 938 cm⁻¹ is attributed to Sn-O-Si stretch [6]. The strong absorption peaks at 1029 and 1125 cm⁻¹ are attributed to Si-O bond of polymerized APTES on the surface. NH₃⁺ (protonation of amine) and NH₂ vibrational signals are found at 1486 cm⁻¹ and 1570 cm⁻¹ respectively. These peaks confirm the presence of APTES on SnO₂ after silanization.

APTES film was used as a substrate for the second step of functionalization. The second step of sensors modification is the attachment of a film on SnO₂-APTES, ended with alkyl, acid or ester groups.

Alkyl, acid and ester modified SnO₂ (red, orange and green curves respectively) FTIR spectra presented in Fig. 1 exhibit two peaks at 1547 cm⁻¹ and 1645 cm⁻¹ which correspond to carbonyl stretch mode and N-H bending mode of amide respectively. An additional broad peak between ~ 3000 and ~ 3600 cm⁻¹ corresponds to N-H stretch of amide. These peaks confirm the success of the reaction between amine group of APTES and acyl chloride group and the formation of amide bond. Asymmetrical C-H stretching mode of CH₃ for SnO₂-APTES-alkyl and for SnO₂-APTES-ester appears at 2965 cm⁻¹. The stretching peak of carbon double bounded to oxygen of ester group of SnO₂-APTES-ester is found at 1734 cm⁻¹ (Fig. 1, green curve).

Therefore, FTIR analysis confirms that functionalization is effectively achieved on SnO₂-APTES after reaction with acyl chloride products by showing the presence of ester, acid and alkyl molecules.

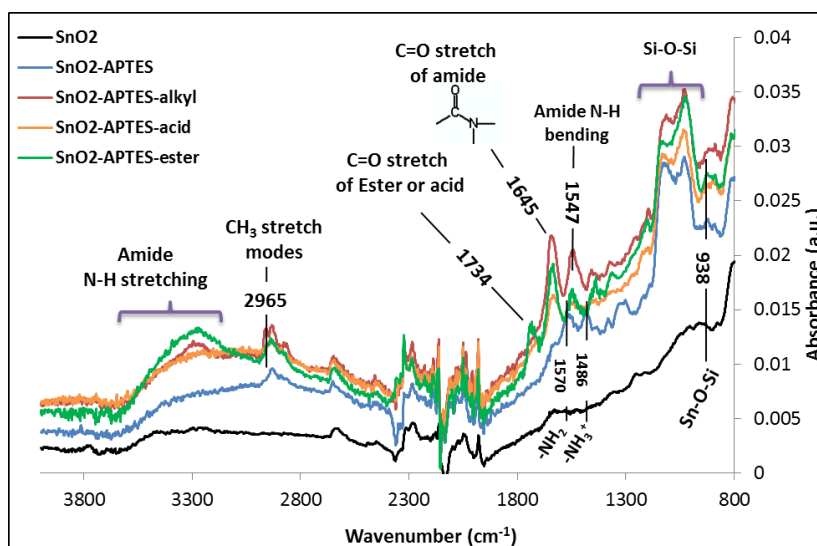


Fig. 1. ATR-FTIR spectra of SnO₂ (black curve), SnO₂-APTES (blue curve), SnO₂-APTES-alkyl (red curve), SnO₂-APTES-acid (orange curve), and SnO₂-APTES-ester (green curve) films.

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 Fig. 2, the sensors were tested to 100 ppm of ammonia balanced with 5% RH air at 25 °C. Figure 2 (red curve) shows that 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. [7] at temperature between 25 to 200 °C.

APTES modified SnO₂ sensor present no change in conductance upon exposure to 100 ppm of ammonia (Fig. 2, dark green curve). 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-alkyl, SnO₂-APTES-acid and SnO₂-APTES-ester exhibit increase in conductance upon exposure to 100 ppm of ammonia gas as presented in Fig. 2. In addition, the response of SnO₂-APTES-ester and SnO₂-APTES-acid are more important than of SnO₂-APTES-alkyl. These responses could be related to the different polarities of the attached end functional groups. Ester and acid are electron withdrawing groups, while alkyl is mostly considered as nonpolar. Ammonia molecule is a nucleophilic molecule (donating). Regarding the interaction between ester and acid from one side and ammonia from the other side, dipole-dipole interaction is taking place. In the contrary, in the case of SnO₂-APTES-alkyl, the interaction is of induced dipole type because ammonia is a polar molecule and alkyl end group is mostly nonpolar. These two interactions (i.e. dipole-dipole and induced-dipole) result in a modification in the dipole moment which changes the conductance of SnO₂. It was reported by B. Wang et al. [3], that the dipole-dipole interaction is always stronger than induced dipole interaction. That is why the response of ester and acid modified sensors is more significant than alkyl one.

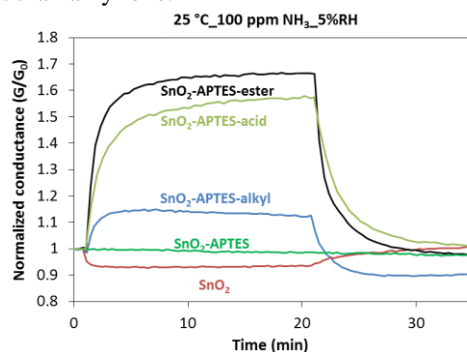


Fig. 2. The sensor response of SnO₂ ($G_0=1.4\times 10^{-5}\ \Omega^{-1}$), SnO₂-APTES ($G_0=7.9\times 10^{-6}\ \Omega^{-1}$), SnO₂-APTES-alkyl ($G_0=1.5\times 10^{-5}\ \Omega^{-1}$), and SnO₂-APTES-ester ($G_0=9.5\times 10^{-6}\ \Omega^{-1}$) to 100 ppm ammonia gas balanced with humid air (5%RH) at 25 °C.

Figure 3 shows that the SnO₂-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. SnO₂-APTES-acid is less selective to ammonia than SnO₂-APTES-ester with respect to ethanol and carbon monoxide. SnO₂-APTES-acid gives response to ethanol and carbon monoxide which are 1.05 and 1.04 respectively. SnO₂-APTES-acid shows no response to acetone gas.

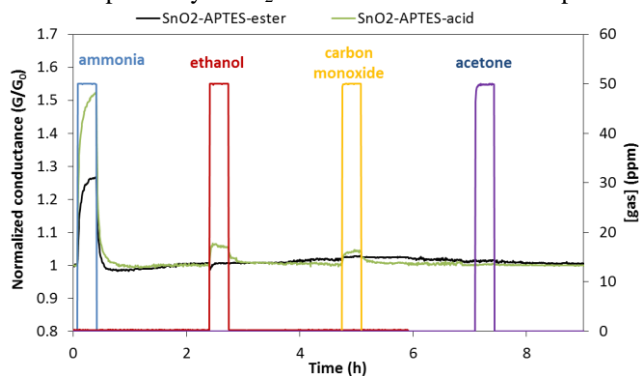


Fig. 3. The sensor response of SnO₂-APTES-ester and SnO₂-APTES-acid upon exposure to 50 ppm of ammonia, ethanol, and acetone gases in air (5%RH) at 25 °C.

4. Conclusion

Molecularly modified SnO₂ thick films were produced by screen printing and solution chemical processes. The functionalized sensors by APTES were used as an amine terminated substrate for modification by alkyl, acid and ester functional groups. Alkyl, acid and ester modified SnO₂-APTES sensors show response to ammonia in the opposite sense with respect to SnO₂. Ester modified sensor is selective to ammonia gas at room temperature with respect to reducing gases like ethanol, carbon monoxide and acetone. **The sensitivity of this sensor in real condition with high humidity level, as well as the detection mechanism will be more deeply investigated in the future work.**

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