"Oral"

Topic 1. Chemical Sensors

Functionalization of APTES Modified Tin Dioxide Gas Sensor

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Summary

In the present work, commercial SnO_2 powder was used for sensor ***thick film*** fabrication. The film was produced using screen printing technology. The **SnO_2** ***functionalization*** was done with 3-aminopropyltriethoxysilane (**APTES**) in liquid phase as an intermediate step, followed by functionalization using hexanoyl chloride exhibiting an alkyl end functional (CH_3) group. The SnO_2 sensor modified with alkyl end group was found to be sensitive to ammonia gas at 100°C. The advantages are the ***reduction of the power consumption*** by decreasing the operating temperature, and the ***enhancement of the selectivity*** and ***sensitivity*** to the gas with respect to pure SnO_2 sensor.

Motivation

Molecularly modified metal oxide gas sensors have shown to be promising devices for selective gas sensor related to disease diagnosis [1]. Those sensors can be used to detect the gas emanated from the human body for breath analysis application. Tin dioxide sensors have lack of selectivity and work at high temperature (350-500°C). The need of selective sensors with high sensitivity at low gases concentration pushes us to modify SnO_2 sensing element in order to change its interactions with gas. The modification with organic functional groups with different polarities change the sensor response to specific gases depending on their polarity [2]. A SnO_2 functionalization based on APTES combined with hexanoyl chloride was investigated. Another objective is to reduce the power consumption by decreasing the operating temperature.

Experimental part

The deposited SnO_2 film on alumina substrate was immersed in a solution of APTES (50 mM) in 95% ethanol, 5 % H_2O mixture at room temperature for 4 h. Then, the APTES terminated SnO_2 sensor was rinsed with ethanol and dried under N_2 flow. SnO_2-APTES sensor was immersed in a solution of hexanoyl chloride (10mM) in chloroform with 5 µL of triethylamine for 7 h. Afterward the sensor was rinsed with chloroform and dried under N_2 flow. The functionalized sensors were characterized by various techniques like attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron microscopy (XPS). Tests under gases were done by stabilizing the sensors under synthetic dry air at 100 °C, followed by injection of different concentrations of NH_3 and acetone gas (3-100 ppm).

Results and Discussion

Figure 1 shows the ATR-FTIR spectra of SnO_2 films after functionalization by APTES and APTES-CH_3. The most important signals characteristic of APTES (figure 1b) are found between 800 and 1800 cm^{-1}. The peak at 938 cm^{1} is attributed to Sn-O-Si stretch [3]. The strong intensity variations between 978 cm^{-1} and 1178 cm^{-1} are attributed to siloxane groups (Si-O-Si) from polymerized APTES.The -NH_2 and -NH_3^+ vibrational signals found at 1570 cm^{-1} and 1496 cm^{-1} (figure 1b) respectively, confirms the presence of amine end functional group of APTES after silanization. These two peaks disappeared and another two peaks at 1547 cm^{-1} and 1645 cm^{-1} (figure 1c) appear after alkyl modification which correspond to carbonyl stretch mode and N-H bending mode of amide respectively.
Figure 2 (a) shows the response (conductance variation) of SnO_2-APTES-CH_3 compared to pure SnO_2 sensor at 100 °C under dry air upon exposure to NH_3 gas. The alkyl modified sensor gives increase in conductance to NH_3, while the non-modified one gives increase in conductance to low NH_3 concentration, and decrease at high NH_3 concentration with unstable base line. We can also notice that the alkyl modified

sensor has relatively faster response and recovery time. Figure 2b shows the relative response ($(G-G_0)/G_0$) versus NH_3 concentration, and points out the high sensitivity of alkyl modified sensor at low NH_3 concentrations (3-20 ppm). Sensitivity at ppb level has to be investigated. Concerning selectivity, the SnO_2-APTES-CH_3 sensor has better selectivity to NH_3 with respect to acetone gas compared with pure SnO_2 sensor (not shown). Assembled polar molecules on a surface of metal oxide semiconductor surface form a dipole layer, which creates a depletion layer on metal oxide surface and adjusts the work function of semiconductor [4]. The alkyl end group (CH_3) is electron donating group. The negative pole of NH_3 molecule, near the molecular layer surface, generates changes in the layer's dipole moment, which implies modifications in the conductance of the whole film.

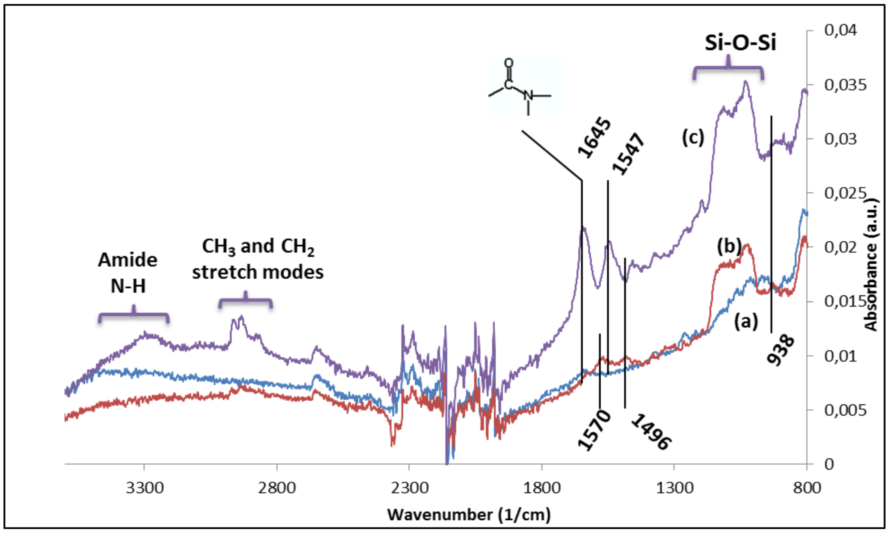

Figure 1: ATR-FTIR spectra of SnO_2 (a), SnO_2-APTES (b), and SnO_2-APTES-CH_3 (c) films.

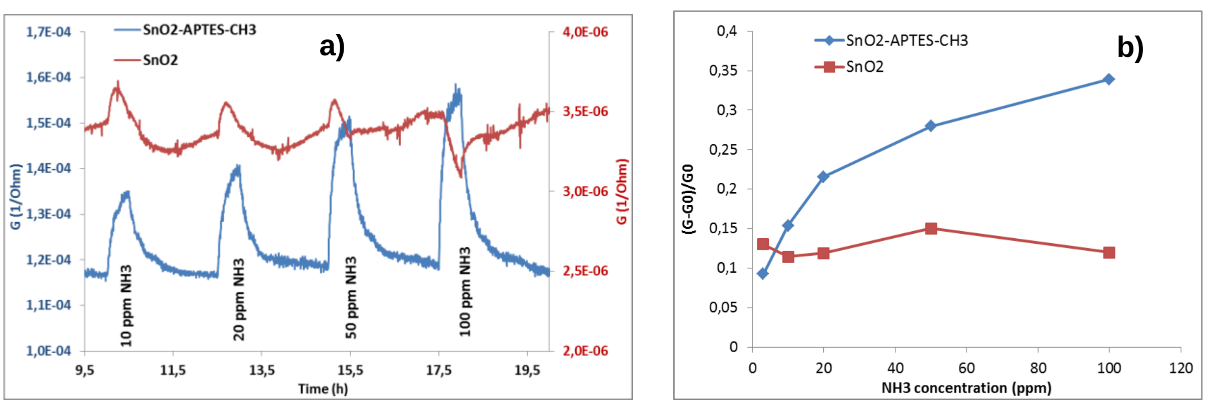

Figure 2: *Response (a) and relative response (b) of SnO_2-APTES-CH_3 and SnO_2 sensor upon exposure to NH_3 gas in dry air. The sensors operating temperature is 100 °C.*

References

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