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Ethanol and H_2S gas detection in air and in reducing and oxidising ambience: application of pattern recognition to analyse the output from temperature-modulated nanoparticulate WO_3 gas sensors

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Abstract

Ethanol and H_2S, mixed with air or NO_2, were detected using a novel nanocrystalline WO_3 sensor produced by advanced gas deposition and operated in a dynamic mode effected by square voltage pulses applied to its heating element, thereby modulating the operating temperature between 150 and 250 °C. The sensor signals were decomposed by fast Fourier and discrete wavelet transforms, and the ensuing data were used as inputs into various pattern recognition methods for identification and quantification purposes. We were able to show that ethanol and H_2S could be detected with good sensitivity and selectivity in the presence of both reducing and oxidizing gases.

Keywords: Gas sensor; Temperature modulation; Fast Fourier transform analysis; Wavelet analysis; Pattern recognition; Tungsten oxide; Nanoparticle

1. Introduction

Even though the olfactory system of humans is exceptional at detecting and identifying many odours, most hazardous gases or vapours can only be recorded at too high concentrations or cannot be detected at all. Standardised methods for ambient air determination involve the use of various techniques and technologies as well as expensive and bulky equipment. All of the methods require laboratory procedures incapable of obtaining real-time results. However, serious attempts to control pollution demand that emissions of hazardous gases into the atmosphere be continuously monitored. Classical analytical methods are not suitable for such real-time analysis, and it follows that there is a need for developing rugged, reliable, small, and inexpensive equipment for air quality monitoring.

Metal-oxide semiconductor gas sensors represent one option for constructing gas monitors. They operate on the principle that the sensor's resistance changes in the presence of reducing or oxidising gases [1]. Although the analysis of single gases and multi-component mixtures by using metal-oxide-based semiconductor gas sensors has been the subject of research for more than 20 years, a number of problems associated with this approach remain unsolved. For example, it is well known that metal-oxide-based gas sensors suffer from drift and lack of selectivity [2], which explains why they are presently used only in low-cost, alarm-level gas monitors for domestic and industrial application [3].

The limited selectivity of semiconductor gas sensors can be evaded in several ways, and a number of different strategies—all having been applied with limited success have been reported. A recent approach consists of analysing the sensor's dynamic response in order to obtain a new set of parameters specific to the investigated gases, one easily implemented method being based on changes in the operating temperature for generating suitable response transients [4]. The required modulation can be obtained by applying a variable signal to a heating element in contact with the sensor. The objective of the temperature modulation is then to alter the kinetics of adsorption and desorption reactions that occur at the sensor's surface in the presence of gaseous species. Previous work of this kind has shown that a modulation of the sensor's working temperature leads to

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a response pattern that is characteristic for the gas under investigation [5–8].

The most commonly used method to extract important features from response signals of temperature-modulated gas sensors is the fast Fourier transform (FFT). An alternative way for decomposing a signal into its constituent parts is the discrete wavelet transform (DWT). The main difference between the two methods is that DWT provides both frequency and temporal information of the signal, while FFT gives only frequency information for the complete duration of the signal so that the temporal information is lost. The ensuing data are used as inputs into various pattern recognition methods for identification and quantification purposes.

The FFT and DWT coefficients provide 'fingerprints' that are characteristic of the concentration level and gas measured. They depend on the chemical reactions that take place between the active film of the sensor and the gas and are, thereby, directly influenced by the characteristics of the active material used and its deposition method. Thus, another important requirement for enhancing the selectivity is the availability of very accurately controlled preparation techniques for the sensor material. Such techniques should be able to provide the desired oxide composition at a minimum number of processing steps. In practice, selectivity is achieved by enhancing gas adsorption or promoting specific chemical reactions via catalytic or electronic effects using bulk dopants, surface modification methods, or by addition of metallic clusters or oxide catalysts [9,10].

In general, sensitivity is improved by microstructural changes such as the reduction of the oxide particle size to the nanometre scale [11] and nanostructured materials are recognised as essential for achieving high gas sensitivity. These materials present new opportunities for enhancing the performance of gas sensors as a consequence of their large surface area and because a significant fraction of their atoms reside at grain boundaries [12,13]. Prior work has shown that the sensitivity of semiconductor oxide materials has been improved by reducing the particle size, and greatly improved properties have been reported for sizes in the 5–50 nm range [14,15].

In the present paper, we detect ethanol and H_2S mixed with dry air or NO_2 using a novel nanocrystalline WO_3 sensor (thickens about 20 μm) produced by advanced gas deposition. The sensor was operated in the dynamic mode effected by square voltage pulses applied to its heating element, thus modulating its temperature between 150 and 250 °C. The sensor signals were decomposed by the FFT and DWT transforms, and the features extracted were used as inputs into various pattern recognition methods for identification and quantification purposes. In particular, unsupervised and supervised pattern recognition methods, specifically principal component analysis (PCA) and discriminant factor analysis (DFA), as well as neuronal networks, specifically fuzzy ARTMAP and radial basis functions (RBF), were applied to distinguish the investigated gases. Furthermore, a linear multivariate statistical algorithm, specifically partial least squares (PLS), was used to build predictive models for ethanol and H_2S concentrations both for pure and mixed gases, and fuzzy ARTMAP and RBF neural networks were also implemented for identifying the class of concentration to which each measurement belonged. The results obtained have shown that ethanol and H_2S gases can be detected with good sensitivity and selectivity in the presence of both reducing and oxidising species.

2. Experimental

WO_3 nanoparticle thick-film gas sensors were employed for the measurements. The sensor device comprised an alumina substrate (9 mm × 7 mm) with two pre-printed gold electrodes, 0.3 mm apart and 5 mm in length, on the upper side and a Pt heating resistor on the reverse side [16]. The WO_3 nanoparticle film was deposited onto the substrate by using an advanced gas deposition unit (ultra fine particle equipment, ULVAC Ltd., Japan). Further details on this apparatus and on the deposition process can be found elsewhere [17,18]. The deposited film was annealed at 600 °C in air, exhibiting then a monoclinic phase with an average grain size of about 23 nm [17,19]. The WO_3 film was 20 μm thick.

The measurement set-up comprised of a 300 ml test chamber, three mass-flow controllers, and a data acquisition system for recordings in the millisecond range, employed for acquiring the sensor's resistance. The temperature of the sensor was varied between 150 and 250 °C by applying square voltage pulses with a frequency of 36 mHz to its heating resistor. The temperature range and the frequency were optimised for the analysed gases. Synthetic dry air (80% N_2 and 20% O_2) at a constant flow rate of 1 l/min was used as both purging and carrier gas.

The sensor was exposed to controlled concentrations of ethanol (10, 50, and 100 ppm), H_2S (1, 5, and 10 ppm), ethanol + H_2S (10 + 1, 50 + 5, and 100 + 10 ppm), ethanol + NO_2 (10 + 1, 50 + 5, and 100 + 10 ppm), and H_2S + NO_2 (1 + 1, 5 + 5, and 10 + 10 ppm). All concentrations were diluted in dry air. Each measurement was replicated four times in order to obtain representative data. Data acquisition started 3 min before the injection of a gas sample into the airflow and took 20 min to complete. The sampling rate was set to 1.33 s^{-1}, i.e. new data was stored every 0.6 s. For purging of the measurement chamber, each measurement was followed by a temperature treatment at 300 °C for 15 min, and subsequently the sensor, subjected to the voltage pulses, was kept for 1 h in the presence of synthetic dry air for recuperating its baseline resistance.

3. Results and discussion

For assessing the selectivity of the WO_3 nanoparticle gas sensor employed in the measurements, the acquired data