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Response of SnO_2 Thin Film Sensors to the Odors of Parmesan Cheese

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Sol-gel-derived tin oxide thin films were used to fabricate gas sensor devices. Their properties in detecting odors of cheese were examined. Very good sensitivity values were observed with a maximum at an operating temperature of about 300°C, indicating the possibility for the devices to be used as active elements in a sensor of a metal-oxide-semiconductor-based electronic nose in the control process of dairy products. Long term stability measurements were also performed.

1. Introduction

Recently, the evaluation of the freshness of foods has become an important routine field in areas of the food industry, such as food chemistry, food processing and food technology. The most common method of evaluation of the quality of foods is based on the chemical analysis of the products of decomposition, and requires a great deal of time and effort. Some authors have reported the possibility of using gas sensor solid-state devices to monitor the quality of food. Thus the application of metal-oxide-based gas sensors to such tasks as detecting the freshness of seafoods,(1) the vintage wine,(2) the discrimination of different brands of coffee,(3) has been discussed in many papers. However, to our knowledge, no data have been reported about measurements carried out

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on dairy products.

In this work we have analysed the response of tin-oxide-based gas sensors when exposed to the odors of "Parmesan," a typical and famous Italian cheese. The preliminary experimental results that show the capability of these sensors to be employed in a new field of interest in the food industry are reported.

2. Experimental Results

SnO_2 thin films were prepared by means of the sol-gel process in the following way: 12.37 g of $SnCl_4$ (99.99%, Aldrich) was first stirred vigorously with 15 g of isopropanol. A partially alkoxy-substituted tin compound of the type $SnCl_x(OC_3H_7)_y$ was formed in solution with the gradual increase of heat. The solution was cooled to room temperature and a 3.42 g water — 10 g propanol mixture was added to induce hydrolysis reaction. Further dilution with 15 g of butanol followed in order to achieve the desired SnO_2 equivalent wt%. All the processes for the preparation of the sols were performed in a glove box Braun Labstar 50 ($H_2O < 1$ ppm).

Thin films with a thickness of about 100 nm were deposited onto 1 μm roughness alumina substrates (5×7 mm^2) by the spin-coating technique. The films were first dried at 110°C for 30 min followed by baking at 600°C for 60 min. Before coating deposition, the substrates were cleaned, first, ultrasonically with neutral detergent solution followed by rinsing with deionised water and ethanol and by boiling in acetone and isopropanol, respectively. After the deposition, the thickness and surface roughness of the films were measured using the Tencor Instruments profilometer Alpha Step 200.

Two gold strips with a gap width of 3 mm were formed as electrical contacts with the aim of testing the electrical resistance variations in a controlled atmosphere. The area of each contact was 2×5 mm^2. In this way, an effective thin film surface for exposure of about 3×5 mm^2 was obtained. With this configuration of contacts the devices exhibited an electrical resistance on the order of 10^9 Ω at room temperature, as measured by means of a Keithley electrometer 617.

The electrical tests in controlled atmosphere were carried out using a system constructed by us and implemented in our laboratory.[(4)] In addition, in order to study the response of the sensors to cheese odors, a suitable experimental set-up was arranged. The sample was placed onto a temperature-controllable heated stage in a stainless cell. Before starting the measurement, dry air was allowed to flow at a constant rate of 100 sccm. The resistance of the sensor, continuously monitored by a computer, reached a stable value after approximately 3 h. When the electrical resistance was sufficiently stable the flow of dry air was deviated and, before reaching the test cell, was allowed to pass through a test tube in which 50 g of Parmesan cheese was allocated. The dry-air flow acts as a carrier of the cheese odors in the test cell.

3. Discussion and Conclusion

Figure 1 shows the plot of the electrical resistance variation as a function of time when a typical SnO_2 sensor was exposed to the cheese odors. The measurement was performed

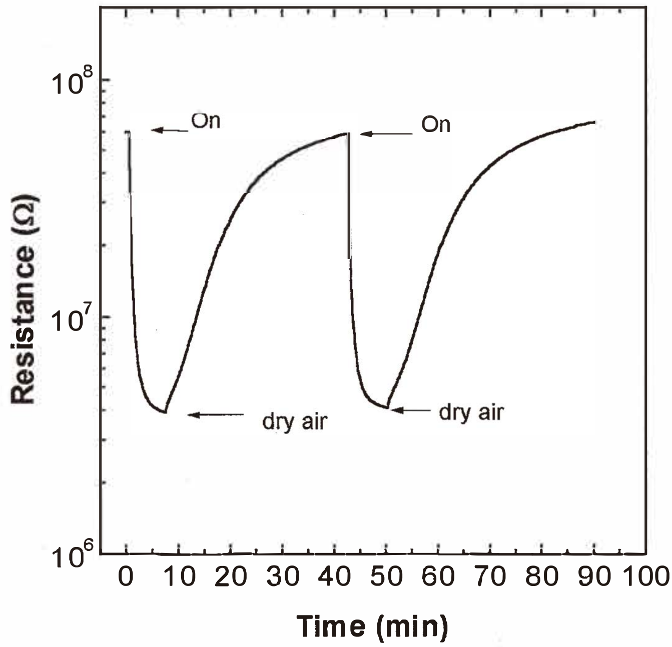

Fig. 1. Typical response of a SnO_2 sensor to the flavours of cheese.

by fixing the sensor operating temperature at 300°C and the test tube containing cheese at 30°C in a thermostatic tank. It is very important to note the reversibility of the response. In fact, as one can see, a sharp drop in the electrical resistance occurs when the odors reach the test cell. The response is very strong and it covers almost two decades. Furthermore, the electrical resistance returns to its starting value when only dry air is allowed to flow in the test cell. The sensor also shows a good reproducibility since the variation of the response is small after subsequent exposures. From the long recovery time we can infer that, in this situation, the odor in the closed tube reaches an equilibrium with the headspace, so its concentration should be considered the same in each exposure. By means of a humidity probe we measured the RH% during the exposure to cheese aroma and it was found to be about 70%. Then, we repeated the measurement by using only 70% humidified air as gas to be tested. The sensor response was lower (30% less) than the previous one and then we could conclude that the observed response to cheese exposure, reported in Fig. 1, was really due to the presence in the headspace of a mixture of volatile compounds and 70% humidity. This is not bad because the contribution of humidity could be useful in relation to some applications in food analysis (for example, seasoning of cheeses).

It is common knowledge that metal-oxide-based sensors exhibit an optimal sensitivity to a specific substance at a certain operating temperature depending on the sensor material to be used and on the gas to be detected. Thus, to obtain more information on the sensing properties further experiments were performed by changing the operating temperature value. The obtained experimental data are reported in Fig. 2 where the electrical resistance variation (in percentage), as a function of the operating temperature is reported for a typical sensor device. As one can see, the plot exhibits a maximum at a temperature of 300°C. The reported sensitivity is related to the quantity $\Delta R/R$ which is given by the relation $\Delta R/R = (R_a - R)/R$, R_a and R the electrical resistance of the sensor before and after exposure to the cheese odor.

Another important parameter to be controlled in testing the reliability of a solid-state sensor device is its stability. Therefore, the ageing characteristics were tested for a period of 2 months. The temperature of the devices was kept constant at the value corresponding to the best sensitivity and the electrical resistance in a continuous flow of dry air was measured. As clearly evident in Fig. 3, within 15 days the resistance slowly decreased by about two orders of magnitude, but after this period of time it seems to reach saturation.

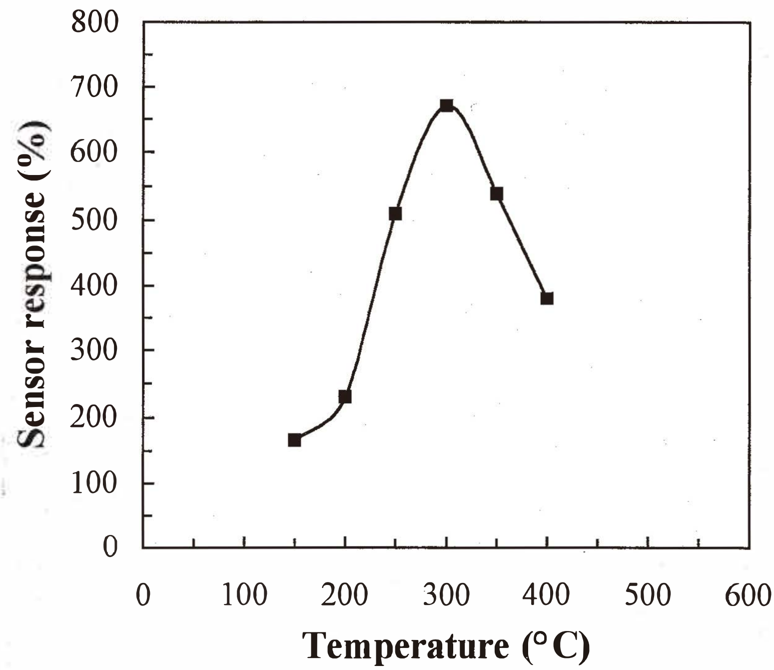

Fig. 2. Electrical resistance variation versus operating temperature for a typical SnO_2 sensor.

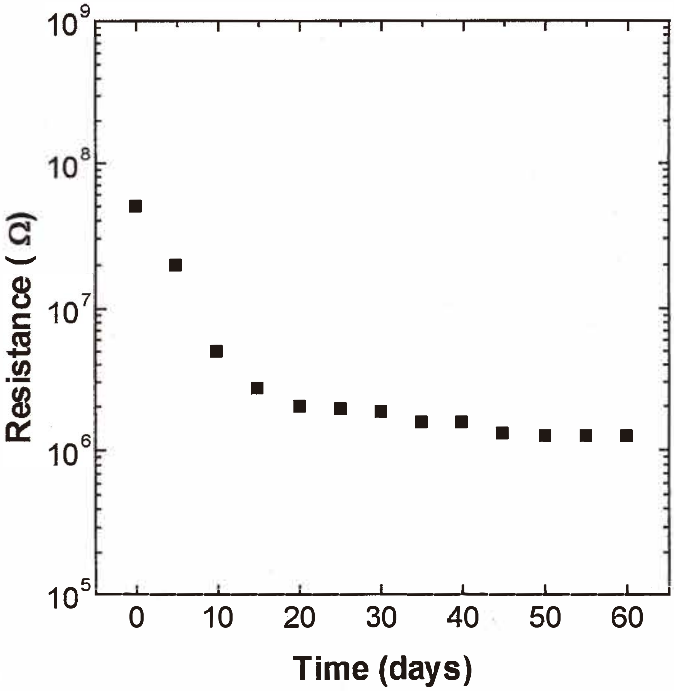

Fig. 3. Dependence of the electrical resistance on the age of the SnO_2 sensor of Fig. 2.

From this point onwards, no appreciable variations were detected and the experimental results showed that both sensitivity and electrical conductance are sufficiently reproducible during tests. Small deviations were sometimes observed after stabilisation, but we believe these to be due to variations of the atmospheric temperature and humidity which might influence and change the physical condition of the sensors and the odors.

The results obtained prompted us to analyse the sensor behaviour after ageing of the piece of cheese. In fact, we performed a sensor test after 30 days, when the surface of the sample in the closed tube was covered by cheese mould. In Fig. 4 the results of a repeated response pattern of a measurement performed in the same experimental conditions as in Fig. 1, but for a different smell (that due to the mould) are reported. As one can see, the sensor response is still good and reproducible, but the sensitivity differs, being lower than the previous one. However, the baseline shows some drift, probably due to the not completely saturated resistance in the conditioning ambient before starting the measurement. Furthermore, one can observe that the response is sufficiently rapid, but a long time is required to reach the starting stationary value; this is more evident in the last measurement in the figure, where we allowed the sensor to recover for a longer time.

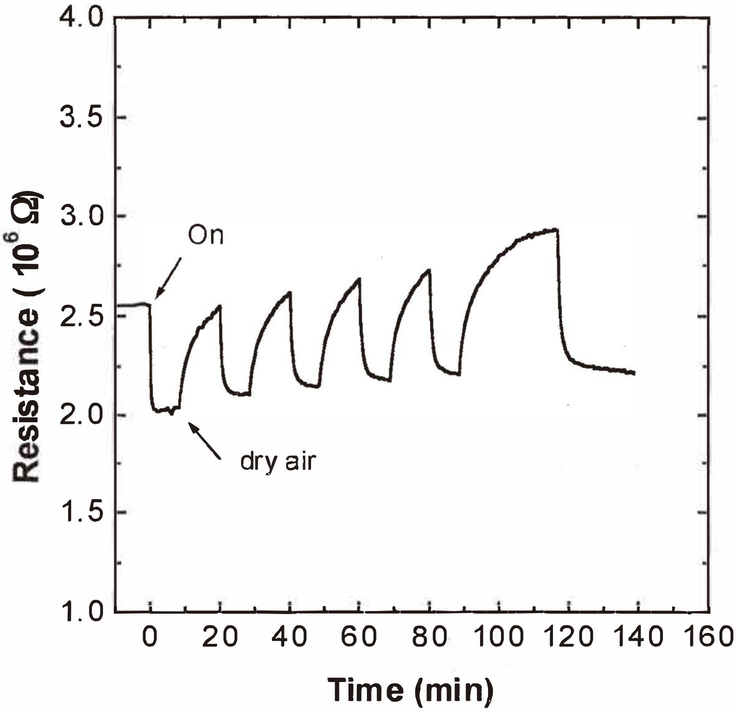

Fig. 4. Response of the same sensor as that in the case of Fig. 1 to the mouldy cheese.

Clearly, one can say that the change in the response could be derived from the different value of the electrical resistance after 30 days of ageing, as evident from the plot in Fig. 3. For this reason, we exposed the sensor to the same amount of freshly cut Parmesan (without mould), but in this case we obtained a response quite different from that in Fig. 4 and with a higher variation in the resistance. Thus we can conclude that the decrease in the sensitivity is due to the presence of mould elements.

In conclusion, for the first time, to our knowledge, we have demonstrated that SnO_2-based thin films could be used for the detection of odors of dairy products. The obtained results are encouraging with respect to the possibility of controlling the quality of a variety dairy of products such as cheese, butter and milk. Clearly, much work is still needed to gather more information about the sensing mechanism. It is known that the most dominant substances normally included in cheese odors are volatile organic compounds (VOCs) such as acetone, butanal, 2-butanone, 2-pentanone, pentanal, hexanal, heptanal and 2-heptanone, which, in different concentrations, could influence, for example, the seasoning of cheeses and the quality of other milk products. At this stage it is necessary to calibrate the sensor's response to various single components in such a way as to establish its selectivity and sensitivity to a specific vapour. It is widely reported[5] that a single sensor, although highly sensitive, is not able to distinguish different substances in a mixture, due to the lack of selectivity to individual vapours. Hence, at present, we are considering other SnO_2-based sensors doped with different elements with the aim of fabricating arrays for the discrimination of different VOCs by using pattern recognition methods. Such work is now in progress and will be the subject of the next report. At this stage, the most significant result of the preliminary experiments reported in this paper is related to the possibility of using metal oxide semiconductor thin films as active materials for an electronic nose with the potential for use in controlling the quality of diary products.

Finally, based on results recently reported by many authors,[6–8] we have also demonstrated the possibility of using sol-gel technology as a method of fabricating sensor devices. In fact, it offers some advantages such as a low production cost and the possibility of easily modifying the composition and the structure of the sensors.

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