DOI 10.5162/IMCS2012/P1.0.12

Influence of applied voltage and catalyst layer thickness on SnO_2 hydrogen sensor performance

Arsen Z. Adamyan[1], Zaven N. Adamyan[1], Vladimir M. Aroutiounian[1], KlaraHernadi[2], Zoltan Nemeth[2]
[1]Department of Physics of Semiconductor and Microelectronics, Center of Semiconductor Devices and Nanotechnologies, Yerevan State University, 1, A. Manoukian, 0025, Yerevan, Armenia.
Corresponding e-mail address: aroutiounv1@gmail.com
[2]Department of Applied and Environmental Chemistry, University of Szeged, Rerrich B. tér 1, Szeged H-6720, Hungary

Abstract:
The new version of sol-gel derived SnO_2 thin-film hydrogen sensor operating at about two times lower temperature and, respectively, with lower consumed power have been obtained. Besides, relatively low resistance of the sensors resulting due to determination of the Pt catalyst layer optimal thickness allows reliable operation at low bias voltage which promotes stable operation even at high relative humidity conditions. In the present work we have examined changes of the sol-gel derived thin-film hydrogen sensors characteristics with increasing the Pt catalyst layer thickness up to 30 nm. It is shown that many parameters of gas sensors such as consumed power, long-term stability as well as selectivity are improved.

Key words: SnO_2, thin-film hydrogen sensor, catalyst layer thickness

Introduction

Comprehension that the finite nature of fossil fuel resources as well as global climate changes due to the combustion of those fossil fuels generate a need to seek a clean, sustainable energy source for an effective transition to a carbon-lean energy economy [1-3]. Hydrogen has been called the optimal replacement for fossil fuels, particularly in the transportation sector [4]. At the same time, hydrogen along with many advantages for its utilization has a risk of a hazardous event. Therefore, development of reliable, highly sensitive and fast acting hydrogen safety sensors ensuring detection of hydrogen before concentrations rise to hazardous level is much requested because the demand for these sensors and fields of their application enlarge all the time [5-7].

In this direction we have carried out a certain research works. Recently, in [8] we have presented ageing conditions and regimes for developed hydrogen sensor [9] which lead to the stabilization of the sensors parameters in time as well as significant increase in gas sensitivity. On the other hand, the improvement of response characteristics of thin-film hydrogen sensors in many respects depends on the catalyst additives amount, deposition methods and conditions. It is always taken into account that catalyst layer is required for enhanced response characteristics. It can influence on spillover process, modify the space charge region at the surface of sensing semiconductor thin film as well as inter-crystallite barriers. Therefore, a certain optimal value for catalyst layer thickness should exist. E.g., the effect of platinum catalyst clusters thickness on the response of SnO_2 rf-sputtered thin-film sensor for LPG detection was studied in [10], where it was shown that the best response is achieved with the presence of 10 nm thick Pt clusters on SnO_2 surface.

In the present work we have examined changes of the sol-gel derived thin-film hydrogen sensors characteristics with increasing the Pt catalyst layer thickness. It is shown that many parameters of gas sensors such as consumed power, long-term stability as well as selectivity are improved.

Experimental

The samples were prepared according to the sol-gel route with use of sodium stannate as a precursor for SnO_2 sol preparation described elsewhere [9, 11, and 12]. It is known that using of this precursor at definite conditions gives highly thermally stable SnO_2 nanoparticles and mesoporous films on its base. However, several

modifications were made to the process. The substrate chip size was 3×3 mm and the step of the comb-shaped electrodes and the width of the paths was 0.1 mm using developed by us the special adjusting device for implementation of double-side alignment procedure. The thickness of Pt catalyst layer deposited by electron beam evaporation or by ion-plasma assisted sputtering was chosen as high as about 35 nm. Exceeding this thickness of catalyst layer leads to the short circuit of the structure and metallic conductivity. The process was controlled by specially modified in-situ thin film thickness monitoring quartz resonator [13]. After final annealing of the samples with sputtered Pt catalyst layer, the samples were mounted in glass metal case with gold wire bounding. Measurements of electro-physical characteristics of the sensors in air and in air mixture with different concentrations of hydrogen and relative humidity (RH) levels were carried out using developed by us and available in laboratory special setup for gas sensor characteristics measurements [9, 12].

Results and discussions

The higher thickness of Pt catalyst resulted in drastically lowering in resistance of the sensors in air (~10^3 Ohm instead of 10^9 Ohm in the case of Pt layer thickness of 20 nm). As can be supposed, lower resistance of sensors can lead to lower cross sensitivity to environmental relative humidity level. In fact, the study of current-voltage characteristics (CVC) of samples shows that in lower voltages region (≤ 1 V) no humidity influence on sensor operation can be noticed.

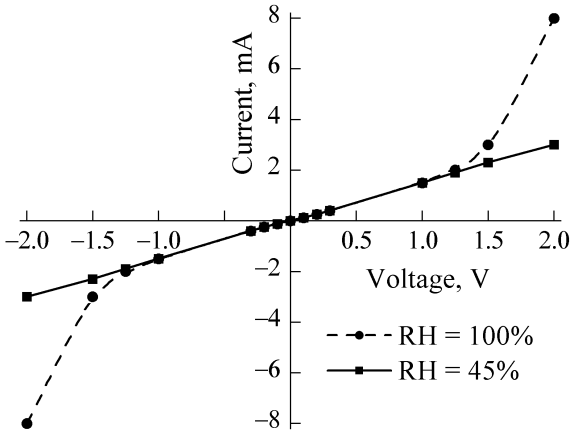

Fig. 1. CVC of the sensor sample at different RH levels. Operating temperature is 20°C.

The results of our more detailed investigations show that humidity does not affect sensor characteristics even after long-term (several days) exposure to ambient with 100% RH level on condition that voltage bias across the sensor does not exceed certain level of about 1 V as it is shown in Fig. 1. Taking into account the latter, the bias voltage across the sensors was selected below 0.3 V.

The obtained results together with technical simplicity of implementing lower resistance precise measurements at low bias voltages lead to significant improvement as opposed to the case of our previous investigations of sensors with lower catalyst layer thickness (and higher resistance), where high humidity levels to a certain extent affected the sensor resistance value in air [7, 9, 14]. We should note that higher bias voltages of about 5 V were used previously in order to ensure measurements of the resistance having values up to 10^9 Ohms with acceptable accuracy.

The response of the sensor was investigated at different operating temperatures starting from room temperature and an optimal operating temperature was selected at the level of 80°C, taking into account many factors, such as sensitivity, response and recovery times, cross sensitivity to humidity level, reversibility of the sensor operation and its overall stability. The last can be seen from Fig. 2, where the sensor sample resistance is plotted versus time during long-term exposure of the sensor into an ambient with 0.5% hydrogen concentration.

Another point investigated is response and recovery times. Let define response or recovery time as the time required for the resistance of the sensor to achieve a level of 70% of corresponding full scale change.

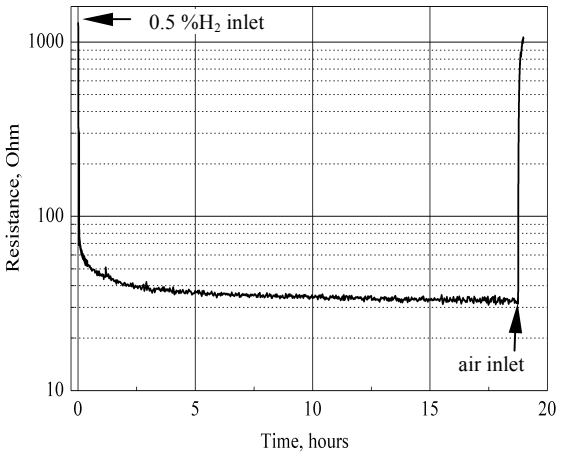

Fig. 2. Sensor sample resistance vs time during long-term exposure to an ambient with 0.5% hydrogen concentration.

The response time in Fig. 2 is about 10s and the recovery time after long-term (19 hours) hydrogen influence is 110 s. It should be noted that during consecutive measurement followed just after long-term experiment (Fig. 3), the response time is the same (10 s), but the

recovery time is 55 s, i.e. twice as shorter. Long recovery time of 110 s in the first case can be explained with deep diffusion of hydrogen gas during long-term exposure.

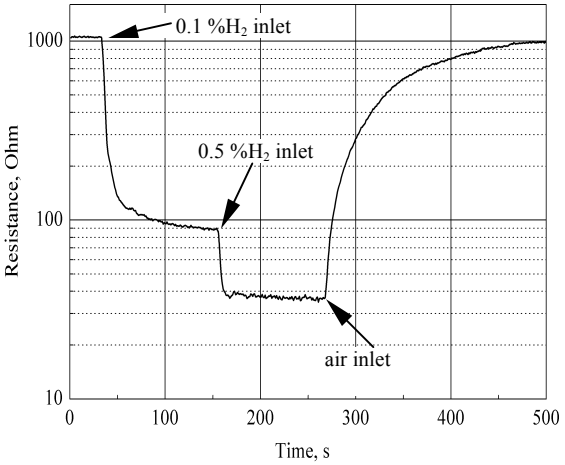

Fig. 3. Sensor sample resistance transients after consecutive 0.1 and 0.5% hydrogen inlets.

Comparing results of two consecutive measurements presented in Fig. 2 and 3, we can notice good reversibility and reproducibility of sensor operation.

As a result of testing of the studied hydrogen sensors during theirs operation under atmosphere contained different gases such as CO, methane, i-butane and other hydrocarbons no cross-sensitivity to these gases was revealed in wide operation temperature range except for i-butane. The sensor reacts to i-butane only in rather narrow temperature range beginning from 180°C to 220°C. At that, the resistance of the sensor changes by below 30% of its value. With the following temperature rise, the sensitivity to i-butane gas also disappears completely.

Conclusion

Thus, as a result of this fulfilled work, the new version of sol-gel derived thin-film hydrogen sensor operating at about two times lower temperature and, correspondingly, with lower consumed power have been obtained. Besides, the low resistance of the sensors allows reliable operation at low bias voltage which promotes stable operation even at high humidity conditions. At that, sensitivity of the sensors is lowered, nevertheless remaining sufficiently high, but the response times are changed negligibly.

The good selectivity of both the suggested low-resistance version of thin-film hydrogen sensors with somewhat thicker catalyst layer and previously developed highly-sensitive hydrogen sensor with lower catalyst layer thickness and higher resistance [8, 9] is observed.

Acknowledgements

This work was partly supported by a grant from Switzerland through the Swiss National Science Foundation (IZ73Z0_128037/1).

References

[1] Midilli, M. Ay, I. Dincer, M.A. Rosen, On hydrogen and hydrogen energy strategies I: current status and needs, *Renewable and Sustainable Energy Reviews*, 9, 255–271 (2005); doi:10.1016/j.rser.2004.05.003

[2] Patrick Moriarty, Damon Honnery, Hydrogen's role in an uncertain energy future, *Int. J. Hydrogen Energy*, 34, 31-39 (2009); doi:10.1016/j.ijhydene.2008.10.060

[3] Carl-Jochen Winter, Hydrogen energy - Abundant, efficient, clean: A debate over the energy-system-of-change, *Int. J. Hydrogen Energy*, 34, S1-S52 (2009); doi:10.1016/j.ijhydene.2009.05.063

[4] Ayfer Veziroglu, Rosario Macario, Fuel cell vehicles: State of the art with economic and environmental concerns Int. *J. Hydrogen Energy*, v.36, 25-43 (2011); doi:10.1016/j.ijhydene.2010.08.145

[5] L. Boon-Brett, J. Bousek, G. Black, P. Moretto, P. Castello, T. Hubert, U. Banach, Identifying performance gaps in hydrogen safety sensor technology for automotive and stationary applications, *Int. J. Hydrogen Energy*, 35, 373-384 (2010); doi:10.1016/j.ijhydene.2009.10.064

[6] William J. Buttner, Matthew B. Post, Robert Burgess, Carl Rivkin, An overview of hydrogen safety sensors and requirements, *Int. J. Hydrogen Energy*, 36, 2462-2470 (2011); doi:10.1016/j.ijhydene.2010.04.176

[7] T. Hübert, L. Boon-Brett, G. Black, U. Banach, Hydrogen sensors – A review, *Sensors and Actuators B* 157, 329-352 (2011); doi:10.1016/j.snb.2011.04.070

[8] A.Z. Adamyan, Z.N. Adamyan, V.M. Aroutiounian, *Int. J. Hydrogen Energy*, 34, 8438-8443 (2009); doi:10.1016/j.ijhydene.2009.08.001

[9] A.Z. Adamyan, Z.N. Adamyan, V.M. Aroutiounian, A.H. Arakelyan, J. Turner, K. Touryan, *Int. J. Hydrogen Energy*, 32, 4101-4108 (2007); doi:10.1016/j.ijhydene.2007.03.043

[10] Divya Haridas, Arijit Chowdhuri, K. Sreenivas, Vinay Gupta I. Effect of thickness of platinum catalyst clusters on response of SnO_2 thin film sensor for LPG, *Sensors and Actuators B*, 153, 89-95 (2011); doi:10.1016/j.snb.2010.10.013

[11] A.Z. Adamyan, Z.N. Adamyan, V.M. Aroutiounian. *Sensors*, 3, 438-442 (2003); ISSN 1424-8220

[12] Arsen Adamyan. Nanostructured semiconductor gas sensors. *Lambert Academic Publishing*, Saarbrücken, Germany, (2010); ISSN 978-3-8433-0068-1

[13] A.S. Stepanyan, A.Z. Adamyan, Deposited thin films thickness measurement and control by quartz resonator method, *J. of Contemporary Physics*, 39, 36-39, (2004); doi:10.3103/S1068337204030077.

[14] A.Z. Adamyan, Z.N. Adamyan, V.M. Aroutiounian, K.D. Schierbaum, S-D. Han, Improvement and stabilization of thin-film hydrogen sensors parameters, *Armenian Journal of Physics,* 2, 200-212 (2009); PACS: 07.07.Df