ATLANTIS PRESS

Advances in Computer Science Research, volume 78

3rd International Workshop on Materials Engineering and Computer Sciences (IWMECS 2018)

Sulfur Mustard Detection with Binary Metal Modification on WO_3, SnO_2 Semiconductor Substrate Surface

Ligong Zhang[1], Shi Gao[1], Xuefeng Wang[1], Shunping Zhang[2], Zheng Du[1], Danping Li[1], Jinxing Yang[1], Rong Zhang[1], Junxiang Chen[1], Wendan Li[1], Yong Xu[1], Guomin Zuo[1, *]

[1]Institute of NBC Defense, Beijing, China, 102205

[2]Huazhong University of Science and Technology, Wuhan, 430074

E-mail: zuoguomin@163.com

*Corresponding author

Keywords: Sulfur mustard, WO_3, SnO_2, semiconductor, binary metal surface modification.

Abstract: In this paper, WO_3, SnO_2 semiconductor materials and their monometallic and binary metal surface modification counterparts was prepared. Resistance-type Sensors were made by MEMS technology and screen printing, whose resistance signals for mustard gas detection were collected by single-chip microcomputer and LABVIEW control soft. Top nine binary metal modification materials were selected out and their best work temperature, ultra violet light irradiation influence, repeatability and stability were researched. Curve fitting equation between top 9 materials S_M and mustard concentration C_{HD} was acquired, which would help us to calculate or estimate the unknown C_{HD} by S_M value from test.

1. Introduction

Resistance of metal oxide semiconductors will have a big change when they are placed in a certain gas atmosphere at a special temperature [1,2]. Based on this phenomenon, Researchers have invented sensors for poisonous gas, inflammable gas and explosive gas et al [3~7]. The popular gas sensitive Mechanism is sample gas reaction involved in different oxygen ion (O^{2-}, O^-, O^{2-}), which is absorbed by semiconductor surface formed by oxygen capturing or losing one or more or less electron form the surface. Electron hole pair was formed in the surface. Electrons were released to the surface from the reaction between sample gas and oxygen ion. Then observable changes in semiconductor resistance were recorded. So we can find and select materials for gas identification and semi-quantitative analysis [8].

Most attention was paid to WO_3, SnO_2 semiconductor materials because of their structure stability, sensitivity, repeatability and long life [9-13]. Based on it, we made monometallic modification and binary metal surface modification. Reaction signals between Mustard gas and the prepared materials were collected and analyzed; it was appreciated that we can select the most suitable materials for mustard gas detection.

2. Experiment

2.1 Synthesis of binary metal surface modification in WO_3, SnO_2 substrate

2.1.1 WO_3, SnO_2 substrate preparation by cotton template

Measuring some $SnCl_2 \cdot 6H_2O$ (or WCl_6), dissolved in appropriate 1,2-Ethanediol (or ethyl alcohol), involved by ammonia, formed suspension. Then, dipped in degreasing cotton and placed in autoclave at a high temperature for a certain time. Washing by water and placed in air oven to dry. Finally, WO_3 and SnO_2 substrate in nanometer size were gotten by calcinations in muffle furnace.

2.1.2 Binary metal surface modification in WO_3, SnO_2 substrate surface

We chose stoichiometric ratio for modification binary metal atom to the substrate W or Sn atom at 0.0025:0.0025:1. Binary metal elements sourced from their hydrochloride or nitrate. Measuring SnO_2 or WO_3 substrate, stirred in water to uniform suspension, then added in binary metal hydrochloride or nitrate drop by drop, last but not least, dried in bake oven. We got the binary metal surface modification in WO_3 or SnO_2 semiconductor, which could be marked by WO_3+Pt+X and SnO_2+Rh+X (X=Rh, Pd, La, Ce, Pr, Sm, Eu, Gd, Ho, Er, Yb, Lu, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Nb, Mo, Ru, Cd, Mg, Al, Ga, Rb, In, Sn, Ca, Sr, Sb, Sc).

2.1.3 Gas sensitive film slurry preparation

Weighing some binary metal surface modification in WO_3 or SnO_2 prepared above, added in organic mixture solvent, and finally treated by ball-milling to slurry.

2.2 Sensor preparation

(1) Platinum slurry was screen printed on ceramic substrate, baked to dry and calcined to form heating Pt electrode, measuring Pt electrode and eight Pt signal electrode. Gas sensitive film slurry was screen printed onto eight signal electrodes, baked and calcined at certain temperature for a certain time.

(2) Then, the ceramic substrate was connected to circuit board by stainless steel bracket, and the whole surface was encapsulated by stainless steel shell whose top was carved in a square hole for UV LED irradiation. Sample gas went through the stainless steel shell from several rectangle narrow channels both in two sides.

2.3 Four-sensor test system setup

Single-chip microcomputer and LABVIEW control soft has been developed to get resistance signals from reactions between sample gases and semiconductor materials. It is very convenient to get signals from 32 materials at once by connecting four sensors together in parallel way in a single test (Figure 1).

Figure 1. The diffusion-way Four Sensor Test system

2.4 Mustard gas dynamic flow generating and quantitative analysis

Mustard gas dynamic flow was generated from a delicate design Purge Gas Generator, which was placed in a temperature-conditioning cold trap. We could get a steady concentration mustard gas flow by controlling the cold trap temperature and the gas ratio between the purge air inside and the diluents air outside. Chemical colorimetric method was used for quantitative analysis for mustard gas flow.

2.5 Sensors' test

Turning on the power supply and running LABVIEW control soft. Calibration curve between resistance and power dissipation was got before test. Then test parameters such as sensors' work temperature modulation and light irradiation modulation was set up. The test condition parameters were shown in talbe 1.

Table 1. HD test conditions

HD ($mg.m^{-3}$)	0.053 0.139 0.478 0.924 1.46
Sensor No.	N_O.1 to N_O.10
Sensor Work temp.(℃)	150、200、250、300、350、400、450、500
Wave of UV LED	365nm (ON or OFF)

3. Results and discussions

We defined some concepts and symbols as follows.

Reaction value S_R, $S_R=R/R_0*100\%$ (1);

Sensitivity value $S=(1-R/R_0)\times 100\%$ (2);

Maximum value of S, $S_M=Max\{S\}$ (3);

Response time of reaction, $t_R=t(S_M)$ - 2min (4);

Recover time of reaction, $t_H= t(S_L) - t(S_M)$ (5)

In above equations, R_0 means the steady resistance even value of the semiconductor exposed at air for 120 seconds. R is the resistance of the material at anytime in the experiment. $t(S_M)$is the time when the S_M happening. $t(S_L)$means that the time of resistance recover to initial value or steady value after changed mustard gas to air flow.

3.1 Reaction with mustard gas in same concentration at different temperature

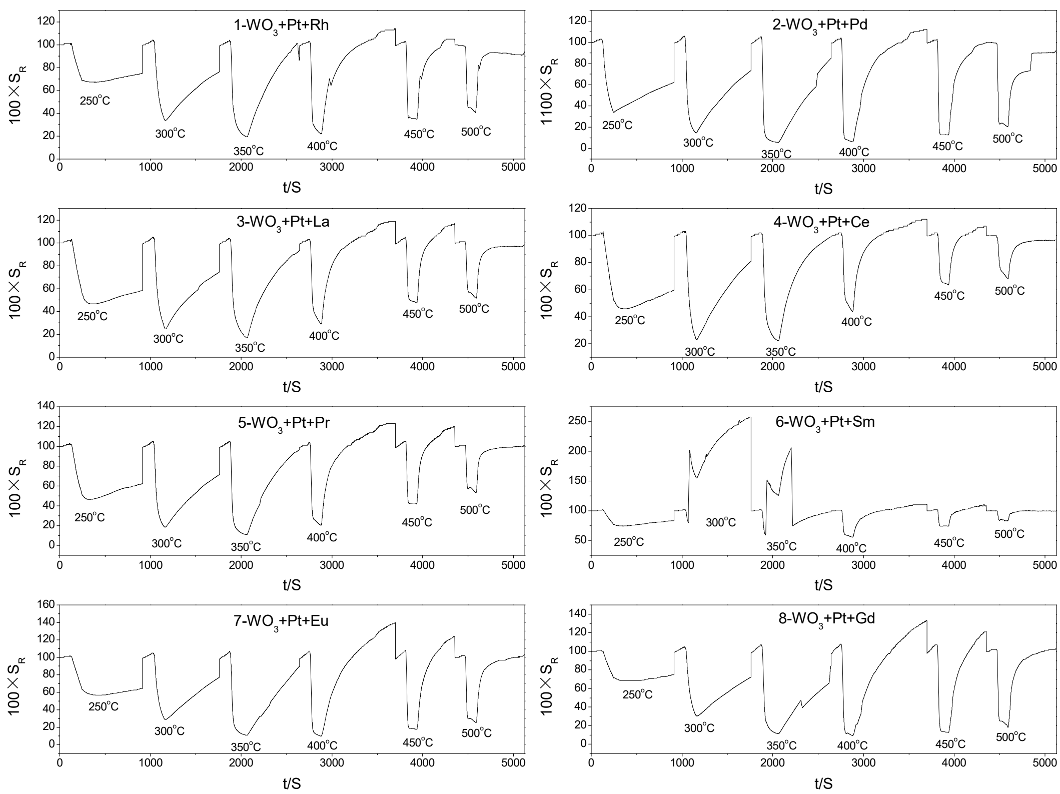

Figure 2. Eight kinds of materials' S_R for No.1 sensor varies with temperature at 1.46 $mg.m^{-3}$HD

As figure 2 shows, eight semiconductor materials of sensor 1 reaction with 1.46 $mg.m^{-3}$ mustard gas. Signals are very well and the sensitive temperature ranges from 350℃ to 450℃.The 3 most perfect materials are 1-2(WO_3+Pt+Pd), 1-8(WO_3+Pt+Gd) and 1-7(WO_3+Pt+Eu), whose best work temperature are all the same temperature 400℃, and their S_M values are 95.9%, 94.1% and 93.2% separately.

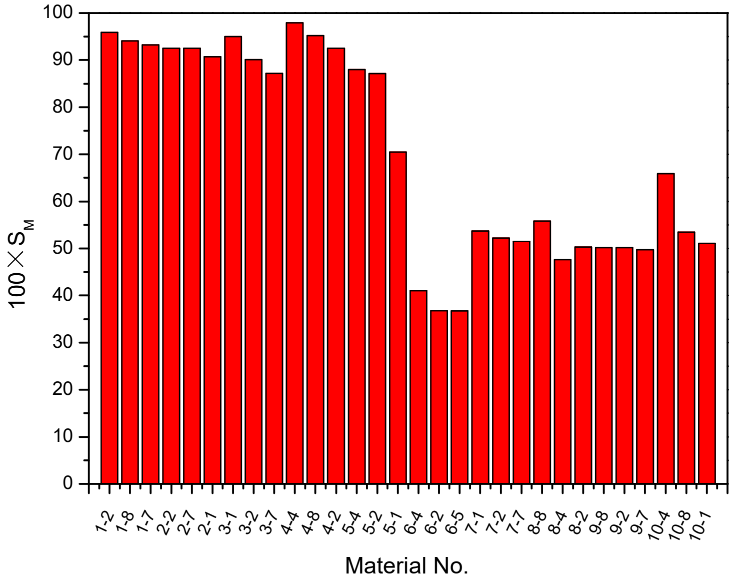

Figure 3. Three best material s' S_M of every sensor at 1.46 $mg.m^{-3}$HD

For the same way, we could get the draws from sensor 2 to sensor 10 in the same condition above. In comparison, 3 biggest S_M values materials of a same sensor are selected, 30 data in a concentration were got 30 data was drawn in a same figure at a same concentration, just as Figure 3 shown due to limited space.

In figure 3, it is easy to find that sensor1 to sensor 5 whose materials are binary metallic modification based on WO_3 substrate is better in detection than sensor 6 to sensor 9, with SnO_2 substrate as basis. Sensor1 to sensor 5 is also better than sensor 10, whose materials are monometallic modification on WO_3, ZnO substrate or pure In_2O_3. The phenomenon is also kept in different mustard gas concentration from 1.46 to 0. 053$mg.m^{-3}$. So, we can conclude that binary metallic modification based on WO_3 substrate is more applicable than those based on SnO_2 counterpart.

Table 2. Best work Temperature of selected top 9 materials

Material No. t/℃ C_{HD} /$mg.m^{-3}$	3-1 M+Fe	1-2 M+Pd	4-8 M+Sn	1-8 M+Gd	4-4 M+Al	1-7 M+Eu	2-7 M+Cr	4-2 M+Cd	3-2 M+Co
0.053	350	350	350	350	350	300	350	350	350
0.139	400	400	350	400	350	400	400	350	350
0.478	400	350	350	400	350	400	350	350	350
0.924	400	400	400	400	350	450	350	350	350
1.46	400	400	350	400	350	400	400	350	350
notes	M=WO_3+Pt								

Taking reaction signals in low mustard gas concentration into primary consideration, 15 best semiconductor materials are arrayed, also in view of factors as tR, tH, the final resistance recovery ratio, the top 9 materials are selected and filled in the table 2. It indicates that the best work temperature for top 9 materials ranges from 350℃ to 400℃, rarely at 300℃ or 450℃. As to different concentration, the best temperature for same material almost keeps a constant value, but as to the same concentration, different materials' best work temperature varies obviously. This just evidently shows performance difference among different materials.

3.2 Top 9 materials reaction with different concentration mustard gas at their best work temperatures respectively.

As shown in figure 4, it is indicated that all reaction signals are the same phenomenon except material 2-7. It increases abruptly with the mustard gas concentration increasing at the beginning stage, and then the increasing velocity slows down as concentration grows to 0. 924mg.m^{-3}. After that, it seems like that seldom increasing occurs when concentration reaches to 1. 46mg.m^{-3}. At the beginning and finishing stages, data distribute relative concentration, but in the middle stage data distribute relative dispersion which could be easy to distinguish.

It is clear that the relationship between S_M and C_{HD} could be described by rational equation. The fitting curve fits origin data very smoothly, as shown in figure 5. So we can calculate the unknown mustard gas concentration the by equation function quickly as soon as we get the S_M value by test.

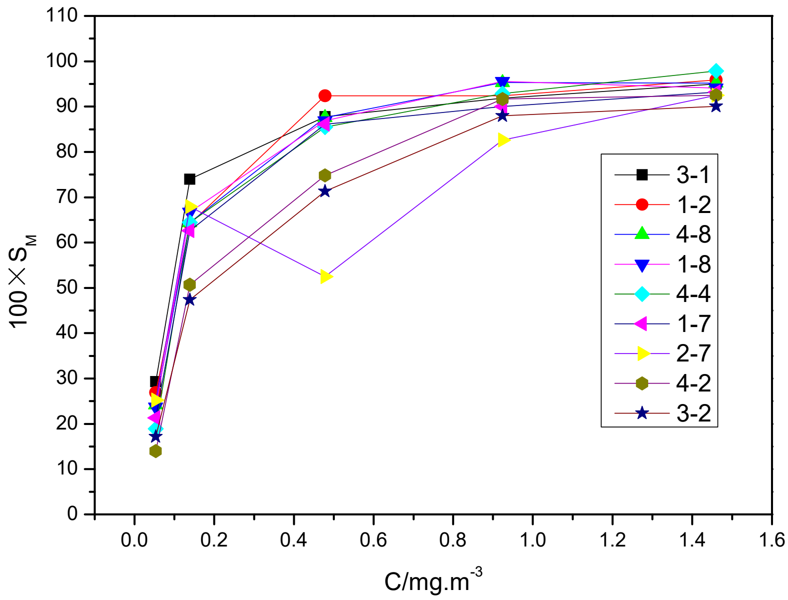

Figure 4. Selected top 9 materials best reaction with HD

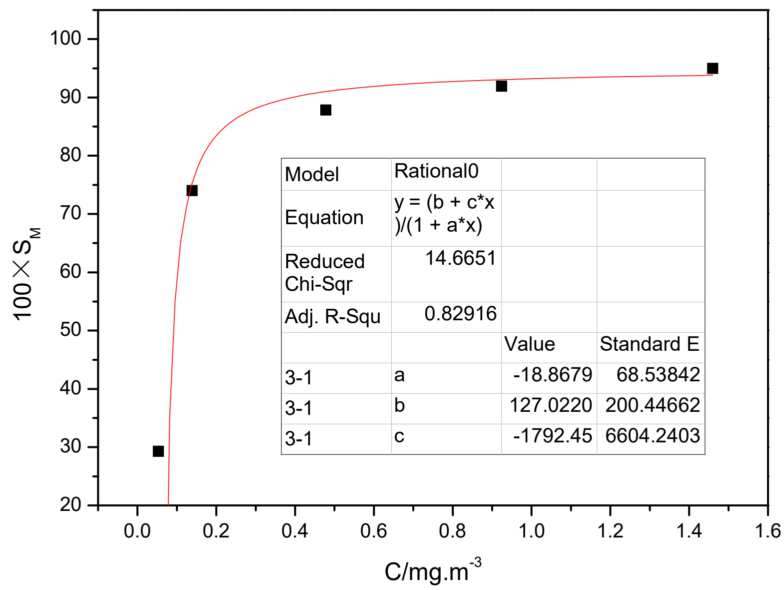

Figure 5. Material 3-1 data fitting curve and original value

3.3 Ultra Violet light irradiation impact on reaction signals

Irradiation by UV LED or not rarely impact on the reaction signals for material 3-1 in high concentration (marked by “0”). But the situation is very different when it comes to middle or low concentration. S_M decreases marked as “-” and S_M increases marked as “+”. Three biggest S_M decrease (marked by “- -”) materials are 1-2,1-8 and 4-8, whose decrease value are 34.5% to 23.8%, 22.9% to 10.7% and 28.6% to 23.9% respectively. The biggest S_M increase (marked by “++”) material is 3-2, whose increase value is 17.8% to 30.8%, followed by material 4-2, whose increase value is from 28.7% to 31.1%.

Table 3. UV LED impact on HD detection SM for selected 9 materials

Material No. t/℃ C_{HD} /mg.m^{-3}	3-1	1-2	4-8	1-8	4-4	1-7	2-7	4-2	3-2
0.053	-	- -	- -	- -	+	- -	- -	0	+ +
0.139	-	-	+	-	+	-	-	+ +	+
0.478	+	0	+	+	+	+	+ +	+	+ +
0.924	0	0	0	+	0	0	0	0	+
1.46	0	0	0	0	0	0	0	0	0

3.4 Repeatability

Taking 1-2 material 5 cycle test at 0. 053mg.m^{-3} mustard gas as an example, S_R fluctuated in 5%. Besides, other 8 materials keep the same way in repeatability. So we can say all top 9 materials have a well repeatability.

3.5 Stability

Material 1-2 had been tested in similar concentration after preparation for 0, 6 and 12 months separately. Longer time after preparation, S_M decreases very slowly. Material 1-2 S_M decreased smaller than 7.3% after 12 months, with all other top 8 materials S_M diminished less than 10.0% for the same time. So, top 9 semiconductor materials keep a stable reaction signals in a year.

4. Conclusion

On the basis of result and discussion, we can conclude as follows.

(1) Top 9 semiconductor materials were selected from 80 ones to detect mustard gas with best work temperature between 350℃ to 400℃.The best temperature for a same material is uncorrelated with mustard gas concentration. Top 9materials have perfect repeatability (less than 5% S_M fluctuation) and long-term stability (less than 10% S_M decrease in a year).

(2) We got the relationship between top 9 materials S_M and mustard gas concentration C_{HD}, depicted by curve fitting function equation, which could help us to calculate the unknown C_{HD} by S_M value from test.

(3) Binary metallic modification based on WO_3 substrate is more applicable than those based on SnO_2 counterpart for mustard gas detection.

(4) UV light of 365nm wave length irradiation has not impact on high concentration mustard gas; when it comes to low concentration, the light makes a biggest increase in S_M by 13.0% for material 3-2 and a biggest decrease in S_M by 12.2% for material 1-8.

Acknowledgements

The research was funded by National Key Research and Development Program of China (Project No. 2016YFC0801301) and Natural Science Foundation of China (6167031847).

References

[1] Seiyama T, Kato A, Fujiishi K, et al. A New Detector for Gaseous Components Using Semiconductive Thin Films. [J]. Analytical Chemistry, 1962, 34(11):1502-1503.

[2] Lee J H. Gas sensors using hierarchical and hollow oxide nanostructures: Overview[J]. Sensors & Actuators B Chemical, 2009, 140(1):319–336.

[3] Lee C S, Choi J H, Park Y H. Development of metal-loaded mixed metal oxides gas sensors for the detection of lethal gases [J]. Journal of Industrial and Engineering Chemistry, 2015, 29: 321–329.

[4] Xie C, Xiao L, Hu M, et al. Fabrication and formaldehyde gas-sensing property of ZnO–MnO_2, coplanar gas sensor arrays[J]. Sensors & Actuators B Chemical, 2010, 145(1):457-463.

[5] Zhang L, Gao Z, Liu C, et al. Synthesis of TiO_2 decorated Co_3O_4 acicular nanowire arrays and their application as an ethanol sensor[J]. Journal of Materials Chemistry A, 2015, 3(6):2794-2801.

[6] Xu L, Chen W, Jin L, et al. A novel SnO_2 nanostructures and their gas-sensing properties for CO[J]. Journal of Materials Science: Materials in Electronics, 2016, 27(5): 4826-4832

[7] Zhao Y, He X, Li J, et al. Porous CuO/SnO_2 composite nanofibers fabricated by electrospinning and their H_2S sensing properties[J]. Sensors & Actuators B Chemical, 2012, 165(1):82–87.

[8] Gurlo A, Riedel R. In situ and operando spectroscopy for assessing mechanisms of gas sensing[J]. Angewandte Chemie International Edition, 2007, (21):3826–3848.

[9] Basu S, Basu P K. Nanocrystalline Metal Oxides for Methane Sensors: Role of Noble Metals [J]. Journal of Sensors, 2009, 29(12):777-790.

[10] Bittencourt C, Llobet E, Ivanov P, et al. Influence of the doping method on the sensitivity of Pt-doped screen-printed SnO_2 sensors[J]. Sensors and Actuators B: Chemical, 2004, 97(1): 67-73.

[11] Korotcenkov G., Cho B. K. Engineering approaches for the improvement of conductometric gas sensor parameters[J]: Part 1. Improvement of sensor sensitivity and selectivity (short survey). Sensors and Actuators B: Chemical. 2013, 188(0): 709-728.

[12] Li X L, Lou T J, Sun X M, et al. Highly sensitive WO_3 hollow-sphere gas sensors [J]. Inorganic Chemistry, 2004, 43(43):5442-5449.

[13] Bae J S, Yun D H, Park C O, et al. Improved selectivity of oxide semiconductor type gas sensor using compensating element [J]. Sensors & Actuators B Chemical, 2001, 75(3):160-165.

The first author: Ligong Zhang (1983—), male, doctor student, lecturer, sensors and toxic gas detection.