KIGAS Vol. 13, No. 2, April, 2009
(Journal of the Korean Institute of Gas)

Characteristics of metal-loaded TiO2/SnO2 thick film gas sensor for detecting acetonitrile

†Young Ho Park · Chang Seop Lee*
Division of Pharmaceutical Engineering,
**Department of Chemistry, Keimyung University, Daegu 704-701, Korea*
(Received 16. October. 2008, Revised 30. March. 2009, Accepted 30. March. 2009)

아세토나이트릴 가스 검지를 위한 센스의 제작 및 특성

†박영호 · 이창섭*
한국국제대학교 제약공학부, 계명대학교 화학과
(2008년 10월 16일 접수, 2009년 3월 30일 수정, 2009년 3월 30일 채택)

Abstract

This study investigated sensitivity of the gas sensor to chemical weapons with the sensor material doped with catalysts. The nano-sized SnO2 powder mixed with metal oxides (TiO2) was doped with transition metals(Pt, Pd and In). Thick film of nano-sized SnO2 powder with TiO2 was prepared by screen-printing method onto Al2O3 substrates with platinum electrode and chemical precipitation method. The physical and chemical properties of sensor material were investigated by SEM/EDS, XRD and BET analyzers. The measured sensitivity to simulant toxic gas is defined as the percentage of resistance of value equation, [(Ra-Rg)/Ra x100)], that of the resistance(Ra) of SnO2 film in air and the resistance(Rg) of SnO2 film in acetonitrile gas. The best sensitivity and selectivity of these thick film were shown with 1wt.% Pd and 1wt.% TiO2 for acetonitile gas at the operating temperature of 250℃.

요 약 - Pt, Pd, In 등의 촉매금속을 사용하여 아세토나이트릴 유독가스에 대한 감도를 향상시키는 SnO2 가스센스에 대하여 연구하였다. Metal-SnO2 후막은 백금전극이 내장된 알루미나 지지체의 스크린법으로 제작되었다. 본 센서의 특성은 검출가스의 농도의 함수로 반응기내 각 센서의 전기적 저항을 측정하여 조사하였으며, 10-50ppm 범위의 유독가스 농도에 대하여 검지 측정하였다. 그 결과 촉매금속의 종류에 따라 센서에서 반응하는 감도가 각각 다르게 선택성을 갖고 있는 것으로 나타났다.

Key words : SnO2 gas sensor, acetonitile, thick film

Introduction

Chemical weapons mean the weapon that can kill all the living organism including mass killing of human lives and plants by using toxic chemicals. The poisonous arrows and spears that the Pygmy tribe in the ancient Africa used are seen as the first real usage of such chemicals in a war. The first time that a chemical weapon was used in a modern combat was when the German army killed 15,000 people by the mass killing chloride gas in the Belgium battle in April, 1915 during the First World War. Starting from this usage, chemical weapons were used 200 times during the First World War resulting in 90,000 casualties.

†주저자:bush777@hanmail.net

The world that witnessed this tragedy agreed up the Geneva Protocol in 1925 that prohibited the usage of toxic chemicals and virus, bacteria. However, even after the Second World War, there have been several hundreds of thousands of casualties through the former USSR's Afghanistan attack and the Iraq-Iran war. In fact, most of the belligerent nations have already developed and stored the prohibited WMD (Weapons of Mass Destruction), and no research related chemical weapons have been released to the public. Especially Korea is the warehouse of explosives that nobody knows when Korea will be drawn into a whirlpool of war due to the fact that it is facing the communist country North Korea. North Korea is ranked the 3rd in the world for the amount of biochemical weapons possession, followed by the United States and Russia. North Korea started to receive the support of the former USSR starting in 1960s; in 1970s, it already possessed the production and launching capability in diverse and unique conditions. According to a real analysis of an information agency of the United States, it is estimated that 4000 metric tons of chemical weapons are enough to kill all 40,000,000 South Korean civilians. A chemical warfare agent means a chemical in a gaseous or liquid state used to give a direct effect on killing human beings, and is represented by choking, blood, blister, and nerve agents. This study is intended to investigate on the early detection of a blood agent[1-5].

In general, HCN (AC), ClCN (CK) are the best known chemicals of blood agents. When exposed, it smells like a seed of a peach. It is a poisonous gas that kills a person within 15 minutes by causing heart suppression, chest pain, convulsion, and coma while being absorbed into the body through respiratory organ. Therefore, the early detection for this kind of human killing gas is very important, and it is essential to maintain the military superiority. Gas sensor has been used in various ways and sensor materials that exhibit the outstanding detection ability for poisonous or highly explosive gas have been used in variety. Most actively studied materials among them are SnO2, TiO2, ZnO2, and WO3 etc. as sensor materials for semiconductors[6,7]. Sensor materials among these are mainly used as mother materials of semiconductor gas sensor. Highly sensitive SnO2 was limited, and the variation in sensitivity was measured by changing composition of TiO2, as an additive material. In addition, in order for study of higher sensitivity properties, catalyst metals such asPt, Pd, In etc., which are sensitive to C-H, a functional group of acetonitrile a simulant chemical gas of blood agents were added[8-9].

Selection of a simulant chemical gas. Blood agents are very volatile and are more stimulating to the respiratory organs, not the blood, as a main location of application poisonous effect. The main reason of blood agent's poison is that it reduces oxygen carrying ability of hemoglobin in blood to stop the metabolism, and that it suppresses the cell oxidation process to kill a person by cell necrosis of neural tissues. Typically it is ok if an adult is exposed to 50-60 ppm for an hour, but it can be deadly if an adult is exposed to a higher concentration for more than 30 minutes. Due to the poisonous effect of blood agents, it is widely used in a capital punishment or assassination. HCN was used for mass killing of Jews by the German solders during the Second World War[10-13]. In this study, acetonitrile gas was selected as a simulant chemical gas.

Acetonitrile gas. Acetonitrile, a simulant chemical gas of HCN, which is known as a blood agent of chemical weapons, is in the liquid state at room temperature. It is volatile without color, but has a fragrant smell such as ether. Acetonitrile has the molecular structure of triple bonds between the methyl group and nitrogen like DPGME(dipropylene glycol methyl ether), and is used as a chemical agent similar to a blood agent. It has TWA (Total Weighted Averages) of 40 ppm, and is known to be deadlier than carbon monoxide[14,15]. It is stable at the STP condition, and produces cyanides, carbon oxides, and nitrogen by heat-decomposition byproduct. In this study acetonitrile gas was selected as a simulant chemical gas of blood agent HCN.

Experimental

Preparation of sensor materials. The sensor material was prepared as the content of TiO2 was changed to 1, 3, 5, 10 wt % with distilled water to the mother material of SnO2 with a magnetic stirrer in order to measure the variation of electrical conductivities in the sensor material. In addition, we went one step forward to add to dope a catalytic metal by the impregnation process to maximize sensitivity and selectivity, which is fundamental condition for gas sensors. A solution is prepared by completely dissolving one wt % of each transition element such as Pd, Pt, and In and the catalytic metal in each beakers by the impregnation process. Catalyst/TiO2/SnO2 powder containing catalytic metals was prepared by stirring each catalytic metal with the magnetic stirrer in TiO2/SnO2 mixture at 25℃. After the slurry is dried at 110℃ for 12 hrs, calcined at 600℃ for 2 hrs, and pulverized in mortar, the final material was be obtained.

Preparation of thick-film sensor material and its structure. For sensor array used in this experiment, a commercial product, whose dimension is 13mm×8mm×0.67mm, has Pt electrode arranged at every 0.5mm on the front of the alumina substrate and a Ni-Cr heater embedded at the back. Before the sensor material is coated on the front of the substrate, it was washed with acetone and then heat-treated at 300℃ to eliminate impurities. Ethylene glycol which plays the role of a binder - ethylene glycol was mixed into the sensor material, kneaded in a slurry condition, and evenly coated with the thickness of 20μm on the alumina substrate by the screen printing method. The sensor material completed by hand was dried at room temperature for 24 hrs, dried at 110℃ for 12 hrs in a high temperature dry oven, and then heat-treated at 600℃for 2 hrs. The schematics of the thick-film sensor alumina substrate and the picture of the substrate after being coated with the sensor material are shown in Fig. 1.[16]

Analysis of sensitivity. A transparent plastic container with volume 10L (250mm×200mm×200mm) was fixed at 50 mm above the ground and sensitivity was measured by adjusting the operation temperature of the gas sensor at 150~350℃ range and the gas concentration at 10-50ppm range. To eliminate the electron or anions inside the sensor material, it was stabilized by treatment at the temperature equivalent to the measured temperature for 12 hrs. After the simulant chemical gas of acetonitrile was injected to the container and the fan started to operate, variations of resistance was measured by a multimeter when the value reached the equilibrium concentration. The sensitivity of sensor was defined as the percentage of electric resistance value equation, [(Ra-Rg)/Ra x100], that of the resistance(Ra) of SnO2 film in air and the resistance(Rg) of the acetonitrile gas. A profile of the schematics of the measuring device of gas sensor used in this study is shown in Fig. 2.

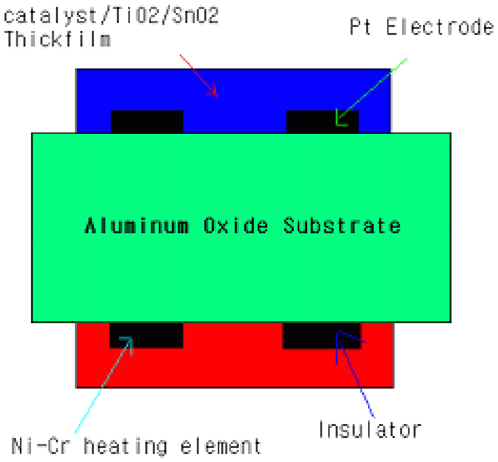

Fig. 1. The schematic view of the fabricated thick film sensor[16].

Results and Discussion

Analysis of sensor materials' properties. Sensor material for gas detection was prepared by differing composition of TiO2 and catalytic metal into mother material, SnO2. XRD, BET, SEM/EDS analyzers

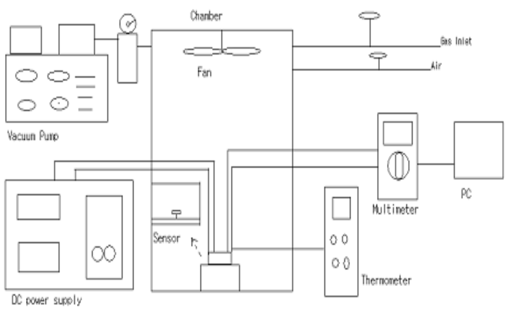

Fig. 2. Apparatus used for gas-sensing experiments.

were used to analyze the particle size, degree of crystallization, the BET specific surface area and the surface particle image condition of each sensor material. First of all, when TiO2 and the metal catalyst were added to SnO2, each pattern of XRD is shown in Fig. 3 and 4. In general, the size variation of particle

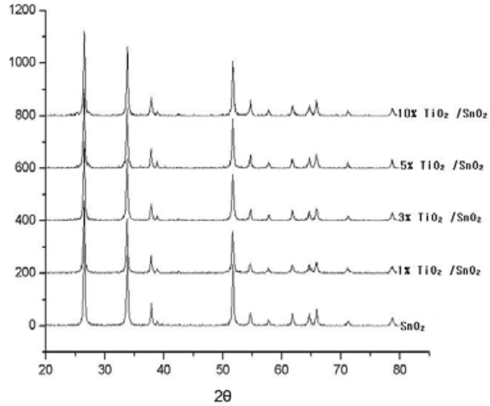

Fig. 3. The X-ray diffraction pattern of 0~10% TiO_2/SnO_2.

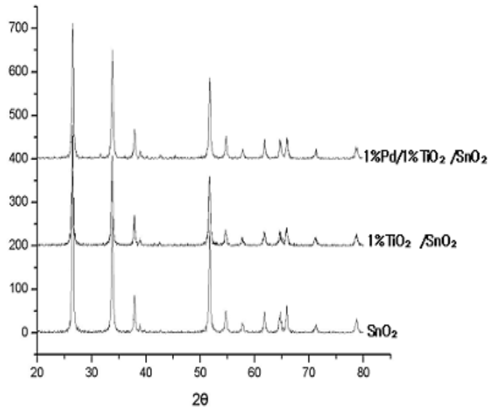

Fig. 4. The X-ray diffraction pattern of catalyst/TiO_2/SnO_2.

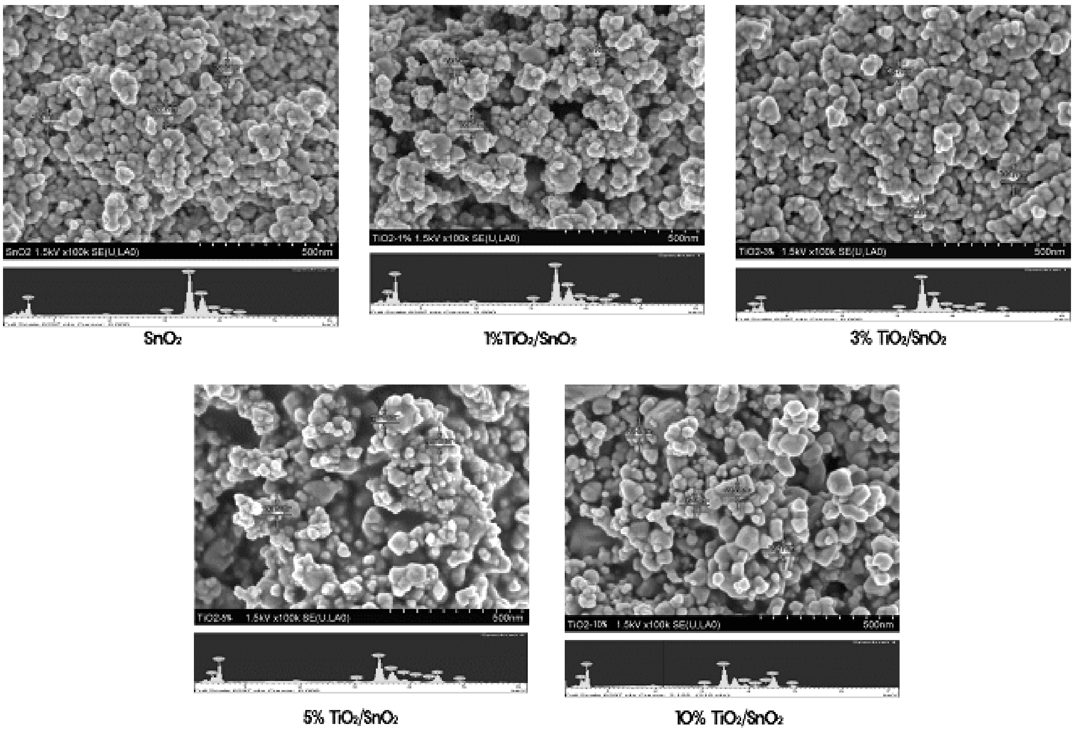

Fig. 5. SEM image of gas sensing material, 1.5kV_100k SE(U, LA0), 500nm.

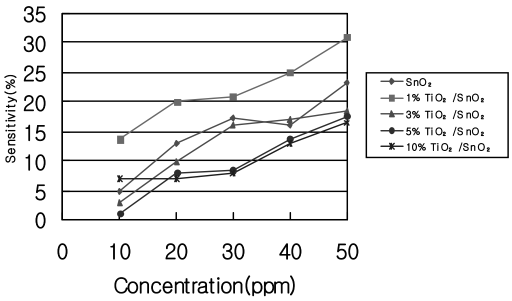

Fig. 6. Sensitivity with amount of metal oxide to the various concentration of acetonitrile gas at 250℃.

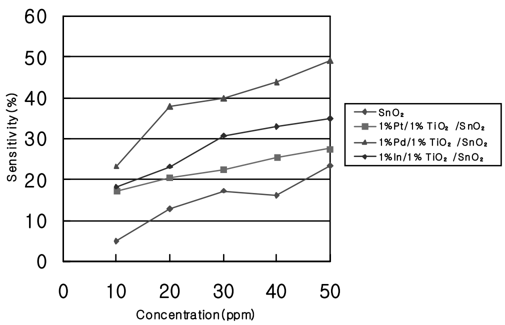

Fig. 7. Sensitivity with catalysts/1wt.% Tio 2/Sn02 to the various concentration of acetonitrile gas at 250℃.

crystallization is the main factor that affects the peak broadening phenomenon in the XRD diffraction. That is, as the size of particle crystallization increases, the range of peak gets narrow. In theory, as the amount of TiO2 in composition increases, the size of the particle becomes smaller and the structure of the phase becomes Rutile. Adding TiO2 contributes to suppressing the growth of SnO2 particle in the calcination process, but the particle grows over a particular content. This is thought to be the result of the aggregation phenomenon, where particles are clumped to each other. According to the Scherrer's equation that represents the sizes of a crystal particle, the smaller the size of particle is, the more the BET specific surface area increases, and therefore, it is thought to contribute to the improvement of sensitivity. Fig. 4 confirms that a new peak of value 2Θ is formed in the specific range of 20 80 as TiO2 and the metal catalyst were added.

Fig. 5 shows the SEM results of each sensor material in an image that TiO2 is added to the mother material SnO2. The particle surface image of each sensor material could be observed by SEM.

Optimal temperature for sensor materials. The property of sensitivity variation for acetonitrile gas at 50ppm, was measured by giving temperature variance of the added sensor material of the metal oxide TiO2 and the metal catalyst to the SnO2 mother material. For a single composition, SnO2 at 300℃ exhibited the best sensitivity, but when TiO2 and Pd was added to SnO2, 250℃ exhibited the best sensitivity. It is speculated that the electron cloud of oxygen anion of atmosphere adsorbed on the surface of sensor material affects the variation in the sensitivity of adsorption and separation at the optimal temperature depending on the contents of metal oxides and the types of catalytic metals. Therefore, in the subsequent experiments the optimal temperature was fixed at 250℃. Sensitivity decreases at the temperature higher than 300℃ again, which corresponds to what Mcaleer and others have reported[17-19].

Gas sensitivity of SnO2 depending on the added amount of TiO2. Fig. 6 shows the investigated result of sensitivity property in the range of 10-50 ppm of acetonitrile gas at various compositions of TiO2 in order to improve the selectivity and the sensitivity of the gas sensor. As can be seen in Fig. 6, sensitivity increases with the increased contents in the variation of the TiO2 composition, and it turns out that the sensitivity was the best when 1 wt % TiO2 was added. It is judged that Ti is substituted to Sn and electron holes on surface are formed in large quantity to decrease electrons contributing to the variation of the electrical conductivity.

Gas sensitivity depending on addition of metal catalysts. Metal catalysts Pt, Pd, and In are doped into TiO2/SnO2 sensor material in order to improve sensitivity and selectivity for acetonitrile gas. It has been reported that the variation of the electrical conductivity is increased by doping metal catalysts into metal oxides and improving separation of absorbed electron clouds of oxygen anion. It is speculated that the effect of this catalysis contributes to improving the electrical conductivity by increasing chemical reactivity which provides variation for the activation energy[19].

Fig. 7 shows the property of sensitivity for acetonitrile gas according to the types of metal catalysts. Various metal catalysts were added with 1 wt % TiO_2/SnO_2 sensor material as the basis. As the Fig. 7 shows, it can be understood that of the sensor material with 1 wt % Pd exhibits more optimal sensitivity than the other metal catalysts. It looks as if the 1 wt % Pd/1 wt % TiO_2/SnO_2 sensor material separates oxygen anion cloud of acetonitrile gas more rapidly than other sensor materials and better selectivity.

Conclusions

In this study, a thick-film gas sensor to detect acetonitrile gas was prepared by having SnO_2 as a mother material and adding various catalytic metals as additives. Sensitivity characteristics of acetonitrile gas depending on added metal oxides and the addition of various metal catalysts, sensitivity characteristics depending on various temperature, and comparison of sensitivity and selectivity with other simulant chemical gaswere investigated. From the above experiments, following conclusions could be obtained:

1. The amount of variation in the electrical conductivity was measured by using the thick-film gas sensor that was reacted to simulant chemical gas.

2. The sensitivity properties of the thick-film gas sensor that TiO_2 and Pd are added to SnO_2 tend to depend on the amount of TiO_2 and Pd, optimum temperature, and the kind of the binder.

3. The sensor material to detect acetonitrile gas shows the best sensitivity and selectivity when the condition is following:

- Optimum temperature: 250℃
- Binder: Ethylene glycol
- Composition: 1 wt % Pd + 1 wt % $TiO_2$with SnO_2 as the mother material

4. The thick-film gas sensor of SnO_2 showed good sensitivity for a little amount of acetonitrile gas, and therefore, it is judged that the gas sensor will be useful for promotion of development technology for the gas fire alarm system that can detect early the poisonous gas that can kill human lives.

Acknowledgement

This work was supported by grant No. RT104-03-02 from the Reginal Technology Innnovation Program of the Ministry of Commerce, Industry and Energy (MOCIE)

References

[1] T. C. Marrs, R. L. Maynard and F. R. Sidell, New York, John Wiley & Sons (1996)

[2] M. Tochigi, T. Umekage, T. Otani, T. Kato, A. Iwanami, N. Asukai, T. Sasaki and N. Kato, Neuroscience Research, **44**, 267-272 (2002)

[3] A. Iwanami, O. Toshiyuki, T. Mamoru, K. Tadafumi, , S. Tsukasa and K. Nobumasa, European Psychiatry, **17**, 199 (2002)

[4] J. A. F. Comptom, Telford Press Caldwell, N. J. USA (1987)

[5] R. L. Maynard, General & Applied Toxology, Mac-Millan, USA 1123-1153 (1995)

[6] Y. Shimizu, N. Kuwano, T. Hyodo and M. Egashira, Sensors and Actuators, **83**, 195-201 (2002)

[7] D. S. Lee, J. K. Jung, J. W. Lim, J. S. Huh and D. D. Lee, Sensors and Actuators, **77**, 228-236 (2001)

[8] P. Gelin, L.Urfels, M.Primet and E.Tena, Catalysis Today, **83**, 45-57. (2003)

[9] S. H. Park, J. Y Ryu, H. H. Choi and T. H. Kwon, Sensors and Actuators **46**, 75-79 (1988)

[10] I. Brewster, J. M. Harrison and L. Leadbeater, Xenobiotica, **17**, 911-924 (1973)

[11] E.C. Rietveld, L.P.C. Delbressine, T.H.J.M. Waegemaekers and B.F Seutter, Architecture Toxicology, **54**, 139-144 (1983)

[12] M. A. Guatelli, Methods in Forensic Sciences, New York, Academic Press, **3**, 233-265 (1964)

[13] Y. Katsumata, K. Sato and M. Oya, et al. Life science**,** **27**, 1509-1512 (1980)

[14] B. Muir, H. B. Duffy and M. C. J. Moran, Chroma. A., 1083, 183-187 (2004)

[15] NIST chemistry WebBook, (2003)

[16] A. Kawahara, H. Katsuki and M. Egashira, Sensors and Actuators, B, **49**273-278 (1998)

[17] B. C. Kim, J. Y. Kim, D. D. Lee, J. O. Lim and J. S. Huh, Sensors and Actuators, B**, 89**, 180-186 (2003)

[18] J. A. Dean, Lange's HandBook of Chemistry, 12th Edition, McGraw Hill, New York, 10-54 (1979)

[19] C. Xu, J. Kurokawa, N. Miura and N. J. Yamazoe, Mater. Sci. **27**, 963-972 (1992)