J. of the Korean Sensors Society
Vol. 13, No. 4 (2004) pp. 143 – 147

Thick Films of $LaNiO_3$ Perovskite Structure Impregnated with In and Bi Oxides as Acetonitrile Sensor

A. V. Salker†, Nak-Jin Choi*, Jun-Hyuk Kwak*, and Duk-Dong Lee*

Abstract

Thick films of $LaNiO_3$ having perovskite structure impregnated with indium and bismuth oxides have been used as sensing material for acetonitrile (CH_3CN) gas. The sensor response for CH_3CN is quite good with an excellent recovery for partial pressure from 3 ppm to 20 ppm between 200 and 250°C. $LaNiO_3$ alone has exhibited low response, but after impregnation of In_2O_3 and Bi_2O_3 have given increased sensitivity even with 3 ppm partial pressure of CH_3CN at 200°C. It is assumed that CH_3CN is undergoing oxidation reaction on surface of the film.

Key Words : $LaNiO_3$, $LaNiO_3$-In_2O_3, $LaNiO_3$-Bi_2O_3, CH_3CN detection

1. Introduction

Perovskites are thermally stable compounds, exhibiting variety of novel properties such as magnetic materials, semi-conductors, conductors, gas sensors and also these are quite resistant to poisoning. $LaNiO_3$ has been tested as a catalyst for a few oxidation reactions and also in some gas sensor property[1]. $LaNiO_3$ adsorbs gases selectively changing electronic property such as resistance and therefore, can be employed as a gas sensing material device. CH_3CN is widely used as an industrial solvent and in chemical intermediates. It is well known toxic as it attacks the liver and blood, leading to many physiological problems. Therefore, early detection of CH_3CN is very important to prevent health hazards.

Xuchen *et al.*[1] investigated sensitivity and response characteristics of the lanthanum nickelate in the exhaust gases of air-propane combustion. Mohan *et al.*[2] reported that $LaNiO_3$ is a p-type with high conductivity at room temperature and its conductivity decrease with a decrease in Ni^{+3} concentration.

In the present investigation, we prepared $LaNiO_3$ perovskite by chemical co-precipitation technique. Metal oxides such as In_2O_3 and Bi_2O_3 were impregnated in $LaNiO_3$ taking 2% of metal by weight employing chemical wet impregnation method. Sensing property to CH_3CN gas was studied over the thick films of these mixed oxides at different partial pressures at varying temperatures.

School of Electronic and Electrical Engineering, Goa University, Goa-403206, India
*Department of Electronic Engineering, Kyungpook National University, Korea

†Corresponding author: ddlee@ee.knu.ac.kr
(Received : February 27, 2004, Accepted : May 17, 2004)

2. Experimental

Nitrate of lanthanum and nickel (AR grade) were taken in stoichiometric molar quantities and dissolved in distilled water. Sodium hydroxide solution (10%) was added drop wise till the precipitation of metal hydroxides (pH 9 – 10) was completed. The precipitate was agglomerated on a steam bath for 3 – 4 h and then 5 ml hydrogen peroxide was added drop wise with constant stirring. The precipitate was filtered, washed several times with distilled water, dried and fired at 700°C for 10 – 15 h in air. This material was characterized by powder X-ray diffraction technique.

Wet impregnation of In_2O_3 and Bi_2O_3 were carried out taking 2% by weight of the metal (In and Bi) in the $LaNiO_3$ perovskite. These compounds are designated as $LaNiO_3$-In_2O_3 and $LaNiO_3$-Bi_2O_3 respectively. A calculated weight of indium or bismuth nitrate was dissolved in distilled water in a beaker and to this solution calculated weight of $LaNiO_3$ powder was added. The mixture solution was stirred continuously on magnetic stirrer. After several hours of stirring the sample was slowly

heated to dryness with constant stirring. The dried sample was heated at 500°C for 4 h in air.

The surface morphologies of the films prepared over silica substrate were examined by scanning electron microscope (SEM ABT DS130C) after gold metallization at 2 mA for 5 minutes.

These compounds were tested as gas sensing materials as devices by preparing thick films employing screen printing technique. The sensing materials were deposited on alumina substrate (0.7×1 cm^2) which contains a heating element on the back side of the substrate. The detailed procedure is given elsewhere[3,4]. After depositing the films, they were dried at 110°C for 24 h followed by firing at 600°C for 1 h and then ageing at 400°C for 72 h. Before testing the sensing property, the resistances of the films were recorded at different temperatures. The sensors were connected with the long bonding pins for electrical conduction and they were mounted on a printed circuit board. The characteristics of the sensor were tested in a testing steel chamber after injecting test gas under study in a continuous flow of synthetic air at different temperatures. The sensor signals were fed to a test system monitored by a PC.

3. Results and Discussion

$LaNiO_3$ was prepared by chemical co-precipitation method and characterized by employing X-ray diffraction technique using Cu Kα target filtered through Ni. The d_{hkl} and relative intensities were in good agreement with those reported in JCPDS file.

Fig. 1 shows the sensor response in air against time as a representative plot for the different partial pressure of CH_3CN on $LaNiO_3$ and impregnated metal oxide

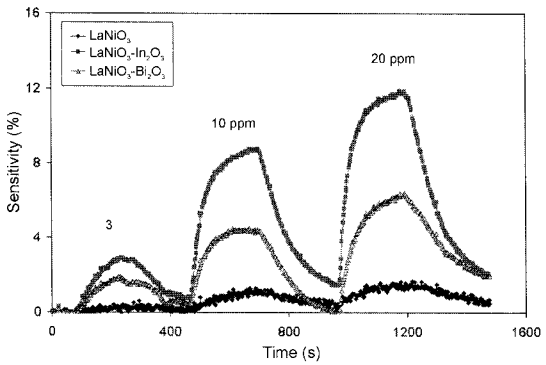
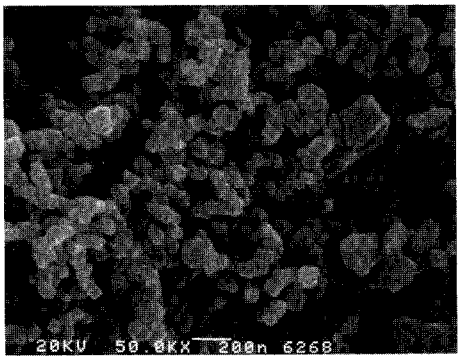
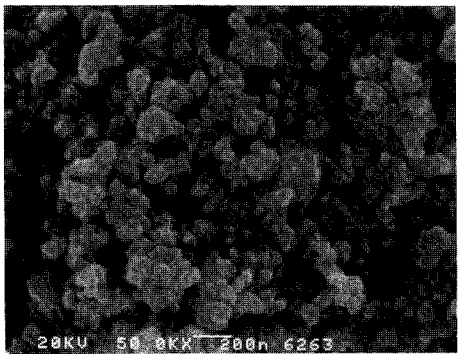


Fig. 1. The sensor response to CH_3CN at 250°C.



(a)



(b)

Fig. 2. Scanning electron micrographs of (a) $LaNiO_3$ and (b) $LaNiO_3$-In_2O_3 thick films.

devices at 250°C. The sensitivity increases with increase in partial pressure of CH_3CN. The test gas was injected for five minutes and allowing three minutes for the recovery of the device before next injection. These devices gave prominent signals of CH_3CN detection without noise, but $LaNiO_3$ showed low sensitivity. The device had good response time and also fast recovery once CH_3CN is removed from the stream gas.

Fig. 2 shows the scanning electron micrographs indicating surface morphology of (a) $LaNiO_3$ and (b) $LaNiO_3$-In_2O_3. It is clear that surface morphology has changed after impregnation of In_2O_3 in $LaNiO_3$. Impregnation leads to agglomeration of particles with more porosity and increasing surface defects to increase more active sites for adsorption and increasing sensor response. The micrographs show the porous crystalline structure with wide distribution of grain sizes ranging from 60 to 150 nm.

Figs. 3 and 4 represent sensor response with partial pressure of CH_3CN on different devices at 250 and

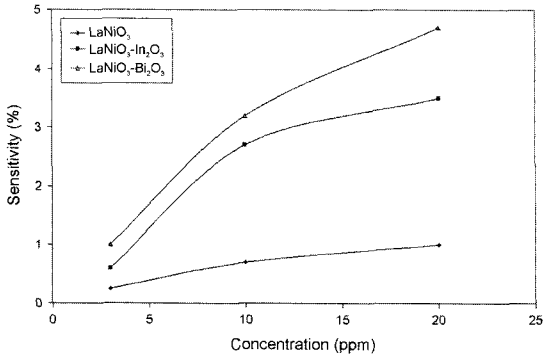


Fig. 3. Sensitivity with respect to concentration at 250°C.

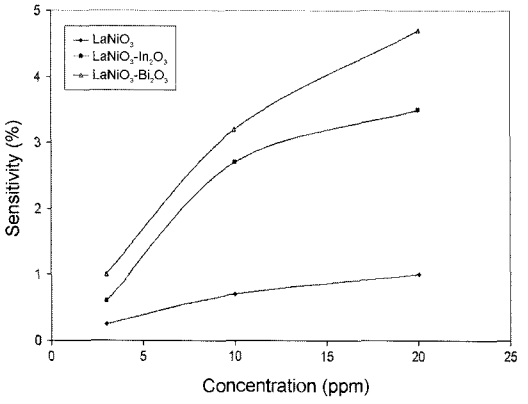


Fig. 4. Sensitivity with respect to concentration at 300°C.

300°C respectively. As the partial pressure increases sensor response increases but the increase is not linear. At 200 and 250°C $LaNiO_3$-In_2O_3 gave higher response followed by $LaNiO_3$-Bi_2O_3 but at 300°C $LaNiO_3$-Bi_2O_3 gave marginally better response than others whereas $LaNiO_3$ showed poor response. Increase in sensitivity by incorporation of In_2O_3 and Bi_2O_3 might have created more active sites on the surface of $LaNiO_3$ which resulted in more adsorption of CH_3CN than $LaNiO_3$ alone.

Fig. 5 depicts the change in sensor response as a function of temperatures on different devices at a partial pressure of 10 ppm. $LaNiO_3$-In_2O_3 showed good sensor response at 200°C but the sensitivity decreases with the temperatures, whereas $LaNiO_3$ and $LaNiO_3$-Bi_2O_3 sensitivities increase from 200 to 250°C and then at higher temperatures fall in sensitivities.

Fig. 6 shows the sensor response as a function of temperature at the partial pressure of 20 ppm CH_3CN. The trend is similar to that of 10 ppm CH_3CN partial pressure. In_2O_3 is well known catalyst for several oxidation reactions and therefore, favouring sensitive response with CH_3CN. However, it is not very active beyond 250°C.

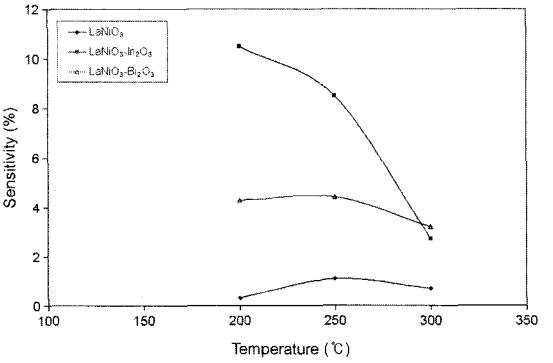


Fig. 5. Sensitivity against temperature at 10 ppm CH_3CN.

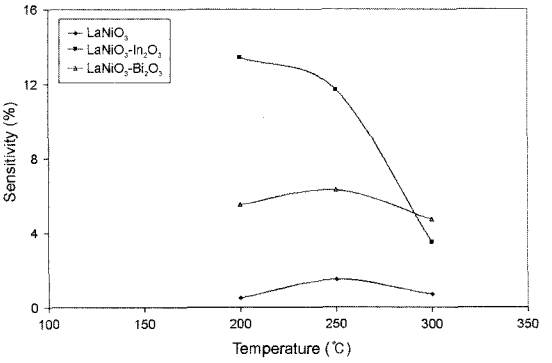


Fig. 6. Sensitivity against temperature at 20 ppm CH_3CN.

Table 1. Resistance of different sensors at various temperatures and corresponding percentage sensitivities for 20 ppm of CH_3CN at that temperatures

Temperature (°C)	19(r.t.)	200	250	300
$LaNiO_3$ R(Ω)	69	65	63	61
$LaNiO_3$ S(%)		0.5	1.5	1.0
$LaNiO_3$-In_2O_3 R(Ω)	369	248	234	198
$LaNiO_3$-In_2O_3 S(%)		13.4	11.7	3.5
$LaNiO_3$-Bi_2O_3 R(Ω)	831	361	304	298
$LaNiO_3$-Bi_2O_3 S(%)		5.5	6.3	4.7

The resistances of different sensors at the sensing temperatures are shown in Table 1. It has been observed that the change in resistance of $LaNiO_3$ is very small with temperatures, whereas changes in resistance in $LaNiO_3$-In_2O_3 and $LaNiO_3$-Bi_2O_3 are significant indi-

cating better semi-conducting properties. In our view, the resistance is not the only criteria for better sensing property, as it is seen that $LaNiO_3$-Bi_2O_3 in spite of higher resistance than $LaNiO_3$-In_2O_3 showed lower sensitivity. Besides resistance there are other factors which influence the sensor response such as active sites, surface morphology or structure, metal oxidation states and surface defects.

Park *et al.*[5] reported a high sensitivity to CH_3CN on Pd doped SnO_2 sensors and they found that CH_3CN decomposes at 130°C producing H_2O, NH_3, CO_2, and N_2O as products. They concluded that the oxidation reaction was dominant for SnO_2 based sensor. It is presumed that CH_3CN adsorbs on the surface of the sensor, reacts with the available oxygen on the surface to get CO_2 and ammonia as the oxidation products. Ammonia may further be oxidized to give products as N_2O and H_2O. $LaNiO_3$ is a slightly oxygen deficient compound and perhaps it is difficult to remove the surface lattice oxygen for the oxidation reaction. When In_2O_3 is impregnated in $LaNiO_3$ activity is increased considerably, probably In_2O_3 can easily furnish its lattice oxygen for the participation in the reaction. Ivanovskaya *et al.*[6] had also reported that the high response of In_2O_3 to reducing gas at high temperature is due to its donation of lattice oxygen.

4. Conclusion

Thick films of In_2O_3 and Bi_2O_3 impregnated in $LaNiO_3$ have been developed for sensing the toxic gas CH_3CN. These fabricated devices have been tested as gas sensors for the concentration range between 3 to 20 ppm and at 200 to 300°C. $LaNiO_3$-In_2O_3 gave better sensor response than others, may be due to the participation of lattice oxygen for CH_3CN oxidation and creating more adsorption sites on the surface. The devices showed good sensor response as well as good recovery after switching off the test gas. $LaNiO_3$-In_2O_3 looks to be more promising and efficient CH_3CN gas sensor material than others at 200 and 250°C.

Acknowledgement

Authors are thankful to Korean Federation of Science & Technology and Confrontation to Chemical and Biological Terror of the Ministry of Science & Technology, for the financial support.

References

[1] L. Xuchen, X. Tingxian, and D. Xianghong, "Preparation and characterization of $LaNiO_3$ A/F ratio sensitivity thin film by sol gel process based on amorphous citrate Precursors", *Sensors and Actuators B*, vol. 67, pp. 24-28, 2000.

[2] R.A. Mohan, L. Ganapathi, and P. Ganguly, "Evaluation of three dimensional character across the $La_{n+1}NiO_{3n+1}$ homologous series with increasing in n^1", *J. Solid State Chem.*, vol. 63, pp. 139-144, 1986.

[3] D.-S. Lee, D.-D. Lee, S.-W. Ban, M. Lee, and Y. T. Kim, "SnO_2 gas sensing array for combustible and explosive gas leakage recognition", *IEEE Sensor Journal*, vol. 2, pp. 140-149, 2000.

[4] N.-J. Choi, T.-H. Ban, J.-H. Kwak, J.-C. Kim, J.-S. Huh, and D.-D. Lee, "Fabrication of SnO_2 gas sensor added by metal oxide for DMMP", *J. Korean Institute of Military Sci. & Technol.*, vol. 6, no. 3, pp. 54-61, 2003.

[5] M. Ivanovskaya, P. Bogdanov, G. Faglia, and G. Sberveglieri, "The feature of a thin film and ceramic sensors at the detection of CO and NO_2", *Sensors and Actuators B*, vol. 68, pp. 344-350, 2000.

[6] H.-D. Park, D.-D. Lee, W.-I. Lee, J.-M. Kim, and J.-M. Kim, "Sensitivity of SnO_2-based thich film devices to CH_3CN", *Sensors and Materials*, vol. 5, pp. 209-220, 1994.

A. V. Salker

- 1979년 Bombay 대학 졸업(공학석사)
- 1986년 I. I. T. Bombay(공학박사)
- 현재 인도 Goa 대학 교수
- 주관심분야 : 재료

Nak-Jin Choi

- [센서학회지 제11권 제5호] p. 30 사진참조
- 1998년 경북대학교 전자공학과 졸업 (공학석사)
- 2002년 경북대학교 전자공학과 박사과정(박사수료)
- 주관심분야 : 전자후각센서 시스템 설계 및 제작 및 산화주석 가스센서 어레이

Jun-Hyuk Kwak

- 1979년 9월 1일생
- 현 경북대학교 전자공학과 석사과정
- 주관심분야 : 산화주석 후막 가스센서 어레이 설계 및 제작

Duk-Dong Lee

- [센서학회지 제11권 제5호] p. 30 사진참조
- 연세대학교 전자공학과 공학박사학위
- 미국 Stanford 대 및 Cornell 대 전기전자공학과 교환교수
- 현 경북대학교 전자전기공학부 교수
- 주관심분야 : 환경가스센서