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Preparation of total VOC sensor with sensor-response stability for humidity by noble metal addition to SnO_2

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Noble metals addition to SnO_2 was examined in order to develop high sensitive total volatile organic compounds (T-VOC) sensors with high stability for humidity. The noble metals loaded SnO_2 thick films were prepared, and their sensor responses were measured for various kinds of VOC gases and a T-VOC test gas. The results of the measurements for various kinds of VOC gases showed that simultaneous addition of Pt, Pd and Au or simultaneous addition of Pt and Au were useful for sensitization for VOC gases giving a small response for the unloaded SnO_2 thick films. These sensors could detect 0.056 ppm of the T-VOC test gas, and the sensor responses increased with increasing the concentration of the T-VOC test gas. The series of additives with Pd was effective to improve the stability for humidity. The sensor loaded with Pt, Pd and Au simultaneously satisfied both high sensitivity to the T-VOC test gas and sensor-response stability for humidity. The results of X-ray photoelectron spectroscopy of the sensor showed that most of loaded palladium exists as PdO. In addition, it was suggested by the shift of binding energy of a Sn3d orbit and an O1s orbit that the electronic sensitization was dominant in the sensor. It was supposed that the electronic sensitization was effective for the sensor response stability for humidity. From these results, the combination of the chemical sensitization by Pt–Au addition and the electronic sensitization by Pd addition gives high sensitivity to the T-VOC test gas and stability for humidity to the Pt–Pd–Au loaded SnO_2 thick films, and it is expected that the SnO_2 thick film with Pt, Pd and Au will be applicable to T-VOC gas sensor.

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1. Introduction

Metal oxide semiconductor gas sensors detect flammable gases by using the change in surface resistance. Many studies have been carried out on the sensing properties with advance in nano-technology, such as minute process technology,[1] precise control of sensor structure,[2),3] improving of sensor responses by additives[4] and development of organic-inorganic hybrid sensor.[5),6] Recently, the number of highly insulated tight buildings has been increased because of the energy saving. This causes deterioration of the air quality and results in inducing sick building syndrome. Because the indoor volatile organic compounds (VOC) concentration is ppb level, the gas sensors detecting ppb level of VOC gases are required to monitor indoor VOC level. However, it is difficult to detect each VOC gas individually. For this reason, there is a view that various kinds of VOC gases all together is considered as total volatile organic compounds (T-VOC) gas.[7),8] We have investigated on the oxide semiconductor thick films suitable for T-VOC gas sensor. SnO_2 was selected as T-VOC gas sensor material, and the sensor response to various kinds of individual VOC gas was examined. The noble metal addition to SnO_2 was useful for the improvement of sensor response to weakly responded gases. Especially, Pd, Au and Pt addition was effective for improving sensor response for aliphatic hydrocarbons, halogenated hydrocarbons and aromatic hydrocarbons, respectively.[9] It is important that sensor responses to weakly responded gases were improved because T-VOC gas contains many kinds of weakly responded gases.[8] In addition, sensor response stability for humidity is also important, because the sensor response of oxide semiconductor gas sensors decreases with increasing humidity in general. The improvement of the sensor response stability for humidity has been investigated on CO sensors.[10)–12] In this study, sensitization of the sensor response to individual VOC gases and a T-VOC test gas as well as the stability for humidity by noble metals addition to SnO_2 were examined.

2. Experimental procedure

SnO_2 powder (NanoTek; C. I. Kasei Co.) was used as a starting material. The average particle size of the SnO_2 powder was approximately 20 nm. In order to prepare the noble metal loaded SnO_2 powder, Pt colloidal solution, Pd colloidal solution and Au colloidal solution (Toda kogyo Co.) were used. The particle size of the noble metal colloid was approximately 2 to 5 nm. The Pt, Pd and Au to SnO_2 ratios of weight were 0.5 wt%, 0.8 wt% and 0.5 wt%, respectively. Noble metal colloidal solution was mixed into SnO_2 powder. In the case of the preparation of SnO_2 loading plural kind of noble metal, each colloidal solution was mixed into SnO_2 powder one after another. The solvent of the mixed suspension was evaporated with stirring for 6 h and then dried at 120°C. The noble metal loaded powders were obtained by grounding the cohered powder. Screen-printable pastes were prepared by mixing the obtained powder and an ethyl cellulose based vehicle. Pt heaters were prepared by screen printing onto Al_2O_3 substrates and firing them at 900°C for 1 h. Au electrodes were prepared by screen printing onto another side of the substrates and firing them at 850°C for 1 h. The noble metal loaded SnO_2 paste was then printed onto the formed Au electrodes. The

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printed SnO_2 paste was dried and fired at 600°C for 1 h. The thickness of the prepared thick films was approximately 15 to 30 μm. The addition of plural kind of noble metals is abbreviated like as Pt–Pd addition. The sensor response for each VOC gas (toluene, heptane, trichloroethylene, acetaldehyde, ethyl acetate, ethyl alcohol and limonene) was measured in a chamber with the volume of 0.064 m^3 (chamber method). The gas sensor was heated at 250°C by the prepared heater on the substrate. The concentration of the gas was adjusted to 1 ppm by evaporation of the liquid reagent whose quantity was calculated from equation of state for an ideal gas. The sensor response for T-VOC test gas was measured at 300°C by a flow method. In this method, regulated concentration of the T-VOC test gas with regulated humidity was flowed with a rate of 200 ml/min. The composition of the T-VOC test gas used in this report is shown in **Table 1**. The composition was determined based on the investigation into the actual conditions of Japanese residences.[7),8)] X-ray photoelectron spectroscopy (XPS; Quantum2000, Ulvac-Phi) was carried out to the SnO_2 thick film with noble metals. The binding energies of each of the spectra were calibrated with C1s at 284.8 eV.

3. Results and discussion

3.1 Sensor response properties of SnO_2 thick film with noble metal addition

Figure 1 shows resistances of the noble metal loaded SnO_2 thick films at 250°C in air. The resistances of the SnO_2 thick films were increased by Pd or Pt–Pd–Au additions, especially in the case of the Pd addition. This should be caused by the decrease in the carrier density.[13)] On the other hand, it is supposed that the decrease in the carrier densities was not caused in the Pt or Au additions. **Figure 2** shows the sensor response of the SnO_2 thick films for various kinds of VOC gases. Sensor responses of the SnO_2 thick film without additives for toluene, heptane, trichloroethylene and acetaldehyde were small. Therefore, a sensitization for these gases is required. The sensor response to heptane was not increased enough in cases of Pt addition, Au addition, Pd addition and Pd–Au addition. Sensor response for heptane was increased in case of the Pt–Pd addition, whereas the sensor responses to ethyl alcohol and limonene were not large enough. The Pt–Au addition and Pt–Pd–Au addition to SnO_2 sensitized for the small response gases like toluene, heptane, trichloroethylene, acetaldehyde all of a kind. The sensor responses of the Pt–Pd–Au loaded SnO_2 thick film to trichloroethylene which is one of the small response gases were measured at 200, 250 and 300°C. The sensor response at 300°C was largest of them. In this study, the measurements of the sensor response to T-VOC test gas were carried out at 300°C. The T-VOC test gas concentration dependence of sensor responses at 50% RH is shown in **Figs. 3**. Figure 3(a) shows the sensor responses of the SnO_2 thick film and the Pt, Pd and Au loaded SnO_2 thick films. Figure 3(b) shows the sensor responses of the Pt–Au, Pd–Au, Pt–Pd and Pt–Pd–Au loaded SnO_2 thick films. All types of the thick films showed distinct sensor response to 0.056 ppm of the T-VOC test gas, and the sensor response was increased with increasing the concentration. In Figs. 3, the Pt–Pd–Au loaded SnO_2 thick film showed the largest inclination. From these results, the addition of Pt–Au or Pt–Pd–Au to SnO_2 is especially effective for sensitization not only to toluene, heptane, trichloroethylene and acetaldehyde as shown in Fig. 2 but also to the T-VOC test gas. The Ministry of Health, Labour and Welfare in Japan has designated the

Table 1. Composition Ratio of T-VOC Test Gas Used in this Study

Components	Concentration (ppm)
Acetaldehyde	0.93
Propionaldehyde	0.22
n-Butylaldehyde	0.50
Decane	0.13
Benzene	0.20
Toluene	0.63
m-Xylene	0.17
1,2,4-Trimethylbenzene	0.17
Ethylbenzene	0.14
p-dichlorobenzene	1.14
Ethyl acetate	1.09
Butyl acetate	0.69
Ethyl alcohol	1.60
2-Propanol	0.12
4-Methyl-2-pentanone	0.20
Acetone	1.75
2-Butanone	0.58
Total	10.29

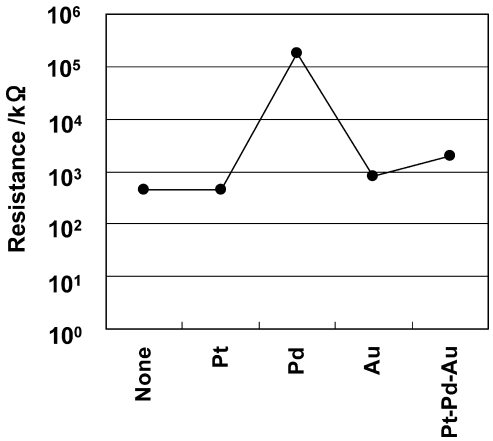

Fig. 1. Resistances of the noble metal loaded SnO_2 thick films at 250°C in air.

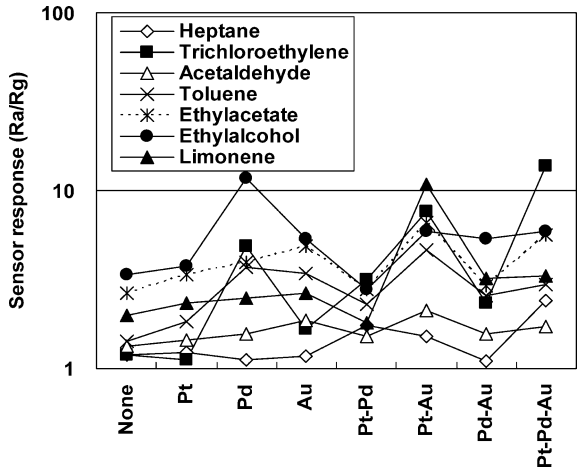

Fig. 2. Sensor response of the noble metals loaded SnO_2 thick films at 250°C for various kinds of VOC gases.

provisional regulation value of T-VOC concentration in an indoor room air to be 400 μg/m^3, which corresponds to 0.112 ppm. From the results of Figs. 3, the provisional regulation value of T-VOC concentration can be detected by using these sensors.

3.2 Improvement of sensor-response stability for humidity

Figure 4 shows relative humidity dependence of the resistance of the thick films in air. The resistances were normalized by the resistance at 25% RH. The trend that the resistances decrease with increasing relative humidity was observed except for the Pd loaded SnO_2 thick film. The decrease in the resistance with increasing humidity should be caused by the adhesion of hydroxyl groups on the sensor surface in the high humidity atmosphere. Because the hydroxyl groups work as electron donors, the resistance decreased with increasing humidity.[11),12)] However, only the Pd loaded SnO_2 thick film did not show the decrease in the resistance at 75% RH. **Figures 5** shows sensor responses to the T-VOC test gas at various relative humidity. The thick films

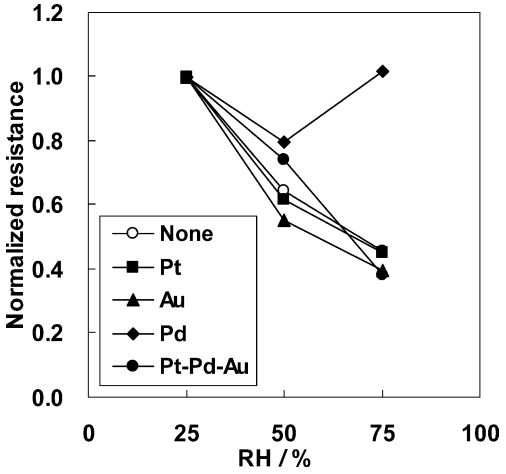

Fig. 4. Relative humidity dependence of normalized resistance of the thick films at 300°C in air.

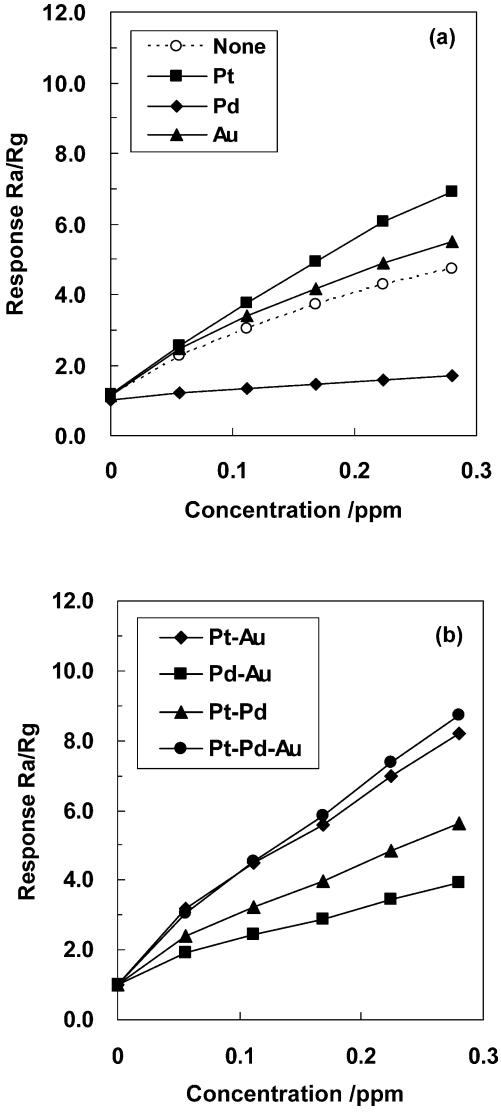

Fig. 3. T-VOC test gas concentration dependence of sensor responses of the (a) SnO_2 thick film and Pt, Pd and Au loaded SnO_2 thick films and the (b) Pt–Au, Pd–Au, Pt–Pd and Pt–Pd–Au loaded SnO_2 thick films at 50% RH.

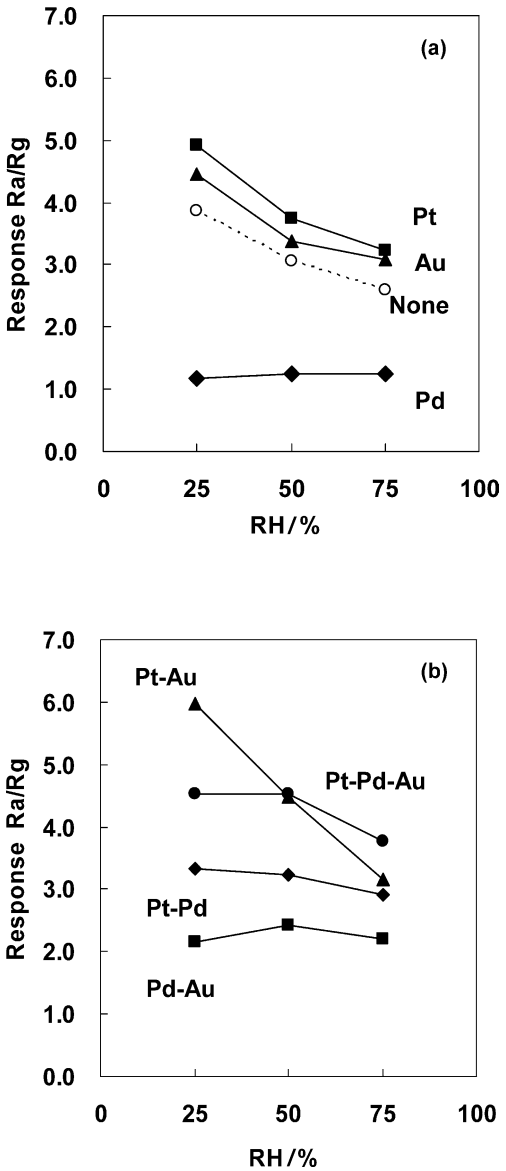

Fig. 5. Sensor responses to the T-VOC test gas at various relative humidity.

containing Pd were superior to the thick films without Pd in a stability of the sensor response for humidity. While the Pt–Au loaded SnO_2 thick films were sensitive at low humidity, the sensor response was decreased with increasing humidity markedly.

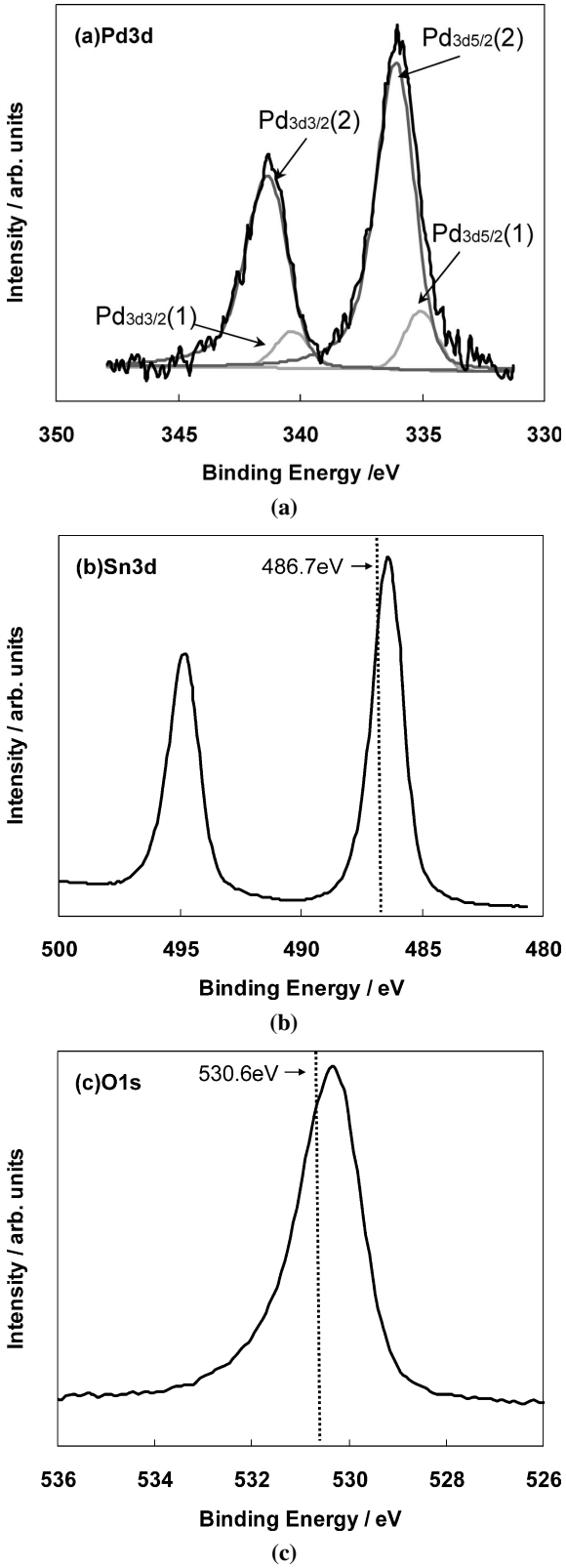

Fig. 6. XPS narrow spectra and curve fitting results of (a) Pd3d orbit and narrow spectrum of (b) Sn3d orbit and (c) O1s orbit.

The sensor response of the Pt–Pd–Au loaded SnO_2 thick films was relatively high and more stable for humidity than that of the other thick films. From these results, the addition of Pt–Pd–Au for SnO_2 is effective for the sensitization to the T-VOC test gas and the improvement of stability for humidity. In addition, it is expected that Pd addition is an important factor for the improvement of stability for humidity. In order to investigate an electronic state of Pd in the Pt–Pd–Au loaded SnO_2 thick film, XPS analysis was performed. **Figure 6**(a) shows XPS narrow spectrum and curve fitting results of Pd3d orbit. The peaks observed at low and high binging energy were corresponded to $Pd3d_{5/2}$ and $Pd3d_{3/2}$, respectively. The peak corresponding to $Pd3d_{5/2}$ was separated to two peaks [$Pd3d_{5/2}(1)$ and $Pd3d_{5/2}(2)$], which were calibrated at a binding energy of 335.14 eV and 336.14 eV, respectively. These peaks indicate the existence of metal Pd and PdO, respectively. Peak area ratio of $Pd3d_{5/2}(1)$ to $Pd3d_{5/2}(2)$ calculated by peak fitting was approximately 1 : 7. Similarly, the peak corresponding to $Pd3d_{3/2}$ was separated to two peaks whose area ratio was approximately 1 : 7. Therefore, most of palladium exists as an oxide state on the surface of SnO_2. This suggests that the high resistance of Pd loaded SnO_2 in Fig. 1 was caused by the existence of PdO formed by an oxygen transport.[13)–15)] Figures 6 also shows XPS narrow spectra of (b) Sn3d orbit and (c) O1s orbit. The intrinsic peak positions of Sn3d and O1s for SnO_2 were 486.7 eV and 530.6 eV, respectively. The peak position of Sn3d and O1s were observed at 0.31 eV and 0.28 eV lower sides from the intrinsic peak positions of SnO_2, respectively. These results show that the electronic sensitization was caused on the Pt–Pd–Au loaded SnO_2 thick films by PdO.[14)] The sensor response stability for humidity could be attributed to the electronic sensitization. Similarly, it is expected to improve the stability for humidity by AgO addition because AgO causes the electronic sensitization, similar to the case of Pd addition.[14),16)] Based on these results, we propose the mechanism about the stabilizing effect for humidity by Pd addition as shown in **Figs. 7**. In the case of the chemical sensitization, such as Pt or Au loading, the hydroxyl groups adhere to the sensor surface in high humidity as shown in Fig. 7(a). Therefore, the amount of adhered oxide on the SnO_2 surface is small in comparison with the case of low humidity, and the decrease in the amount of adhered oxide

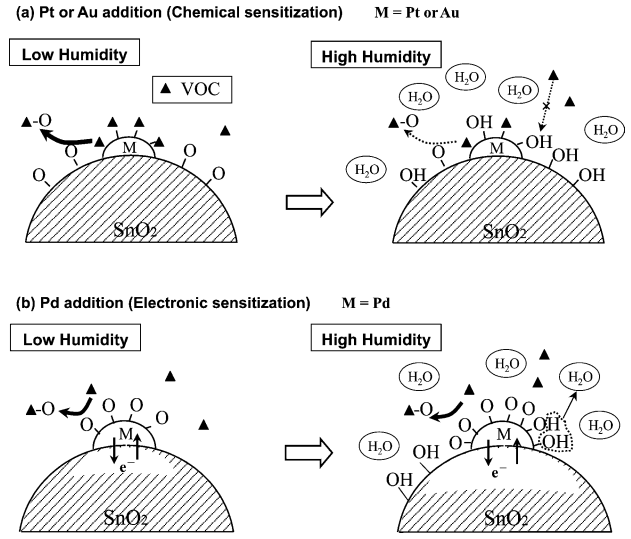

Fig. 7. Schematic images of sensor responses of (a) Pt and/or Au addition and (b) Pd addition under humid atmosphere.

contributes the resistance decrease in Pt or Au loaded SnO_2 thick films in high humidity as shown in Fig. 4. In addition, the adhered hydroxyl group to the loaded noble metal surface interferes the adhesion of VOC gases. The decrease in the sensor response in high humidity is caused by the interference because the adhesion of VOC gases to the surface of loaded noble metal plays an important role in the chemical sensitization. On the other hand, the Pd loaded SnO_2 thick films showed high resistance in high humidity as shown in Fig. 4. The high resistance is attributable to the advance of the oxidation of loaded Pd surface by the adhered hydroxyl groups in high humidity. In the case of electronic sensitization, such as Pd loading, the oxygen on the noble metal surface plays an important role for sensitization. Therefore, the sensor response is stable in high humidity compared to the case of Pt or Au addition. In Fig. 4 and Fig. 5, while the resistances of the Pt–Pd–Au loaded SnO_2 thick films decrease with increasing relative humidity, the response was stable for the humidity. This suggests that the adhesion effect of hydroxyl group to Pt and Au and the sensitization effect by PdO were caused simultaneously in high humidity. The combination of the chemical sensitization by Pt–Au addition and the electronic sensitization by Pd addition gives high sensitivity for T-VOC test gas and stability for humidity to the Pt–Pd–Au loaded SnO_2 thick films.

4. Conclusion

In order to sensitize and improve stability for humidity of the SnO_2-based T-VOC gas sensor, noble metals addition to SnO_2 thick films were examined. The sensor responses for VOC gases and T-VOC test gas are enhanced by the noble metal addition to SnO_2. These sensors can detect 0.056 ppm T-VOC test gas, and the sensor responses increase with increasing the concentration of the T-VOC test gas. The series of Pd addition to SnO_2 are effective for the improvement of sensor-response stability for humidity. It is supposed that the electronic sensitization is effective for the sensor response stability for humidity. The Pt–Pd–Au addition is effective for both sensitization for T-VOC gas and stability for humidity. The results of XPS analysis and sensor response measurements show that the electronic sensitization by PdO is caused in Pt–Pd–Au loaded SnO_2. From these results, the combination of the chemical sensitization by Pt–Au addition and the electronic sensitization by Pd addition gives high sensitivity to the T-VOC test gas and stability for humidity to the Pt–Pd–Au loaded SnO_2 thick films. The Pt–Pd–Au loaded SnO_2 will be applicable to T-VOC sensor.

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