

Effects of nanoadditives on the stability of chemical gas sensors

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Abstract

The effects of dopants and annealing temperatures on the long term stability of the SnO₂-based gas sensors to CO were investigated by doping Pt/SnO₂ nanoparticles with CeO₂, Sm₂O₃ and SiO₂ at 700 and 850°C. Accelerated stability tests were performed by exposing the fresh powders and the fabricated sensors to humid air at 600°C for 15 days. Gas sensing measurements were carried out on the fabricated sensors at the 5th, 9th, 12th and 15th days in addition to the fresh point. CeO₂ and SiO₂ addition were found to be effective in stabilizing the performance of Pt/SnO₂ sensor, while Sm₂O₃ did not have the same effect. Increasing the annealing temperature led to a decrease in sensitivity decline during the exposure period.

Key words: : Dopant, annealing temperature, long term stability, accelerated stability test, gas sensor.

Introduction

Long-term stability is one of the most important factors determining the practical use of the gas sensors. However, it is rarely discussed in the literatures devoted to the chemical gas sensors either from sensitivity or selectivity point of view. It is required for any gas-sensing device to exhibit stable and reproducible signal for the period of at least 2–3 years [1]. Considering this objective, there are some approaches used for stability improvement, such as: utilization of chemically and thermally stable materials, avoiding the use of gas-sensing materials with an extremely small grain size and addition of dopants to the sensing materials followed by optimization of their composition in gas-sensing material [2]. It is inferred that instability in the performance of the metal oxide gas sensor arises from a number of factors such as structural transformation, which may be due to the growth or coalescence of the grains. Korotcenkov et al. [2] found that the change of grain size could be accompanied by the following effects: change of the geometric size of the metal oxide, change of the catalytic and electrophysical properties of the metal oxide layers.

In this work, we used the accelerated stability tests to study the effect of dopants and annealing temperature on stabilizing the performance of Pt/SnO₂ gas sensors.

Experimental

All the sensors were fabricated in thick films, utilizing SnO₂-based sensing materials. SnO₂

was prepared by sol-gel using SnCl₄ as a precursor and doped with 5.0 wt% CeO₂, Sm₂O₃ and SiO₂, followed by 1.0 wt % Pt dry impregnation. The as synthesized powders were dried at 100°C and subsequently calcined in air for 4 h at 700 and 850°C.

In order to investigate the long term stability, the fabricated sensors and their powders were exposed to air with 30–40% RH at 600°C for 15 days under the flow of 20–30 cc/min. The gas sensing measurements to 100 ppm CO at 250°C, were carried out for the fresh sensors and the sensors exposed to the mentioned conditions for 5, 9, 12 and 15 days. The nanoparticles before and after the exploitation period were denoted as "fresh sample" and "aged sample".

The sensing materials were characterized by XRD and BET prior and after the stability tests in order to monitor the morphological and structural changes. XRD characterization was carried out only for the sensing materials calcined at 700°C, while the specific surface area measurements by BET method were carried out for all the sensing materials.

Results

Structural characterization

Based on the X-ray data presented in Fig. 1, the diffraction peaks could be attributed to the crystalline planes of tetragonal cassiterite SnO₂. No peaks corresponding to the dopants' phases was detected, due to their either amorphous

phases and/or too small crystallites sizes to be detected by XRD.

In the case of fresh Pt/SnO₂ and fresh Pt/SnO₂-SiO₂, in addition to the SnO₂ diffraction peaks, low intensity peaks at about 39.8° and 46.38° can be observed, which are ascribed to the Pt (111) diffractions. It is worth mentioning that the corresponding peaks to Pt crystallite phase were not detected any more at the XRD pattern of the aged samples, which may be attributed to the formation of PtO due to the long time exposure to air.

It can also be observed that, for the sample doped with Ce and Si the intensity and width of peaks did not change after the exploitation while for the undoped sample and the one doped with Sm, the changes in these parameters were dominant. In other words, the comparison between the XRD patterns of fresh and the aged samples indicates that, the structure of Pt/SnO₂-CeO₂ was thermally stable while the structure of Pt/SnO₂-Sm₂O₃ was completely different.

The results of BET measurements are presented in Table 1. As is observed no significant particle growth has occurred for the samples doped with CeO₂, Sm₂O₃ and SiO₂ while the size of the undoped particles drastically increased. Comparing the results obtained from BET and XRD, a crucial contrast was reached. In the case of Pt/SnO₂-Sm₂O₃, on the contrary to the results obtained from XRD patterns, which showed a significant crystal growth during the stability test, the growth of

d_{BET} during the exploitation period was not dominant compared to the one for the samples containing other dopants.

Sensitivity measurements

Figure 2 presents the sensitivity of the sensors during the 15 days of stability tests. As is observed the sensors with ceria and silica dopants got stable after the 5th and 12th days respectively, whereas the undoped Pt/SnO₂ and the doped one with samaria did not reach a stable performance during the test period.

According to Fig. 2 Pt/SnO₂ sensitivity drastically decreased during the period of stability test but the reduction trend slowed down from zero point and continued up to the final point. In other words, the major part of sensitivity reduction belongs to the first 5 days of the test period.

Sensitivities of the sensors doped with Cerium oxide got stable after the 5th day of the tests up to the final point. According to I. T. Weber et. al [3] who investigated the effect of noble metals on the structure of Ce-doped SnO₂, Pt diffuses into the SnO₂ lattice and incorporate (participate) into the matrix. Furthermore, CeO₂ stabilizes the location of Pt on the nanoparticles of SnO₂. Sm₂O₃ presence improved the sensitivity of Pt/SnO₂ as a result of grain size reduction and an increase in the height of Schottky barrier. On the other hand, the changes in the responses of Sm₂O₃-doped SnO₂ sensors continued until the end of stability test. It can be concluded that samarium oxide addition did not lead to

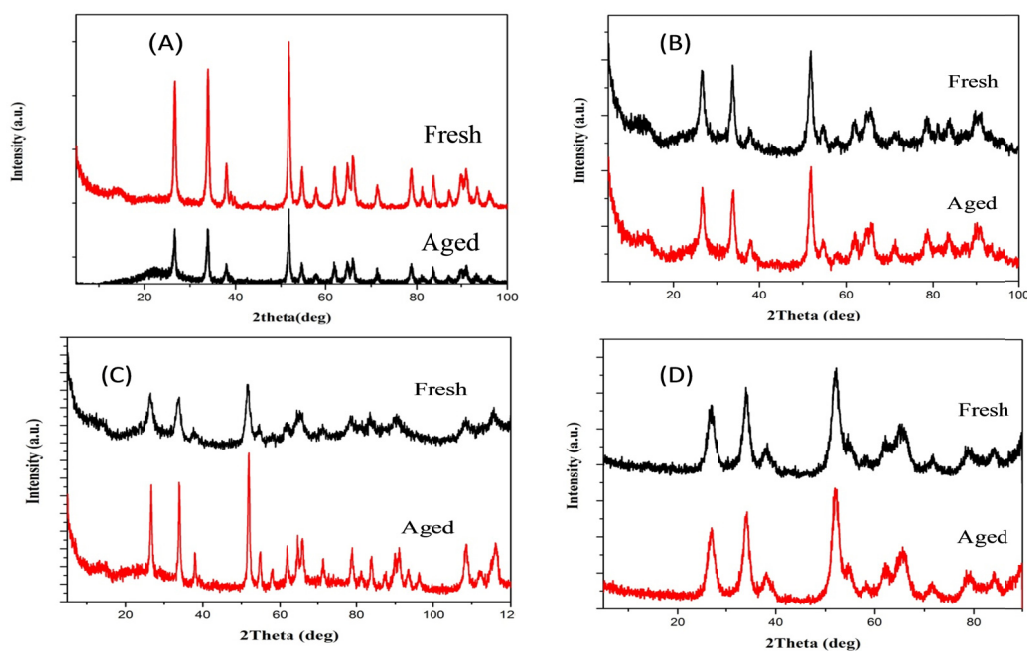


Fig. 2: XRD patterns of fresh and aged (A) Pt/SnO₂ and (B) Pt/SnO₂-Ce (C) Pt/SnO₂-Sm (D) Pt/SnO₂-Si, calcined at 700°C, before and after the exploitation period.

Tab.1: BET specific surface area of fresh and aged samples (before and after the stability tests in humid air at 600°C).

	Calcined at 700°C				Calcined at 850°C			
	Pt/SnO ₂	Pt/SnO ₂ -Ce	Pt/SnO ₂ -Sm	Pt/SnO ₂ -Si	Pt/SnO ₂	Pt/SnO ₂ -Ce	Pt/SnO ₂ -Sm	Pt/SnO ₂ -Si
BET of fresh samples	13	45.5	29	62.6	11.2	12	18.1	36.2
BET of aged samples	12	24.7	26.6	59.2	10.5	11.06	17.8	35.9

stabilization of the performance of Pt/SnO₂ gas sensors.

According to the results shown in Fig 2., silica addition improved the sensitivity. It appears that as long as grain growth is inhibited by interstitial Si, the total resistance is decreased which leads to sensitivity improvement [4]. Through SiO₂ addition, stability in the performance of Pt/SnO₂ gas sensors was observed since the 12th day of the stability test. An increase in annealing temperature decreased the sensitivity decline during the stability tests for all fabricated gas sensors.

Conclusion

In the case of undoped Pt/SnO₂ and doped with sammaria, crystal growth under the condition of stability test were more pronounced as compared to the crystal growth of the ones doped with ceria and silica. Thus, CeO₂ and SiO₂ addition improved the thermal stability of Pt/SnO₂ structure.

It was expected that the samples with long term-stability in sensitivity possessed thermally stable structures and they lost their surface area with a slower pace. According to the report of Nakamura et al. [5] the drift in resistance and sensitivity values was attributed to three factors; grain growth of SnO₂ particles, decrease in water chemisorption and Pt sintering. Therefore, it can be concluded that the interaction between the dopant and Pt particles play a more significant role in stabilizing the performance of gas sensors.

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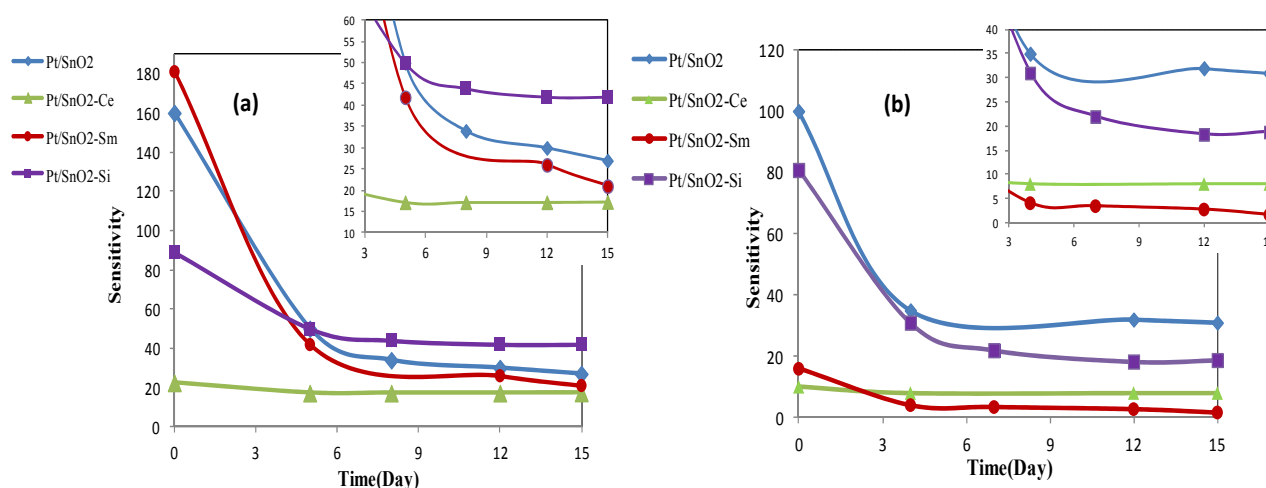


Fig. 2: Gas sensing measurements of the sensors calcined at (a) 700°C and (b) 850°C, during 15 days.

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