Research Report

Development of High-performance Zirconia-based Gas Sensors Using Nano-structured Sensing Electrodes

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The present study is overviewed the recent developments in yttria-stabilized zirconia (YSZ)-based planar sensors using nano-structured sensing electrodes (SE) aiming at sensitive and selective detection of exhaust gases and ammonia slip in automobiles. Particular attention is focused on the fabrication of nano-structured Au-SEs and evaluation of its sensing characteristics in a wide operating temperature range. It was observed that the sensing performance of nano-structured Au-SEs depended to a large extent on the size and shape of Au nano-particles as well as on the morphology of YSZ substrate.

A growing production of automobiles and implementation of industrial combustion furnaces especially in developing countries enforce a strong concern globally on environmental pollution due to release of various hazardous gases (NO_x, hydrocarbons (HCs) and CO). As for the automobiles are concerned, conventional three-way catalyst (TWC) and selective-catalytic reduction (SCR) systems are used to oxidize CO, NO_x and HCs to environmentally safe CO_2, N_2 and H_2O[1]. Thus, the minimization of concentrations of exhausted gases will result in keeping the clean environment and CO_2 reduction. The control of functionality of TWC and SCR systems requires the development of high-performance solid-state gas sensors workable in harsh environments and high temperature.

The yttria-stablizied zirconia (YSZ)-based gas sensors using the different kinds of sensing electrodes (SE) are capable of providing the sensitive and selective responses to various gases. Furthermore, new attractive findings in a field of nano-structured materials allow applying their distinguished features to improve the selectivity and sensitivity to a target gas. In fact, we have recently reported that the YSZ-based sensor attached with Au-SE fabricated by r.f. sputtering (sub-micron Au particles) gave sensitive and selective response to NO_2[2].

Thus, to examine the effect of size and shape of Au nano-particles on its gas sensing characteristics, Au-SEs were fabricated by applying the colloidal gold solution with the particle size of 5 nm on different YSZ plates (porous rough- polycrystalline (rp) YSZ: grain size and roughness of about 300 nm; dense polished-polycrystalline (pp) YSZ: grain size – about 5 μm, roughness – 150 nm; and atomically-smooth single-crystal (sc) (100) and (111) YSZ: roughness is less than 0.5 nm). Figure 1 shows the morphology of Au-SEs fabricated on (a) rp-, (b) pp-, and (c, d) sc-YSZ plates after annealing at 1000°C for 2 h. It was observed that almost all Au colloids diffused into the surface layer of rp–YSZ (Fig. 1, a) and this sensor gave the highly selective and sensitive response to C_3H_6 at 550°C (Fig. 2). Such a behavior is attributed to the formation of intermediate compounds (propylene oxide or acrolein) in the vicinity of nano-Au/YSZ interface with

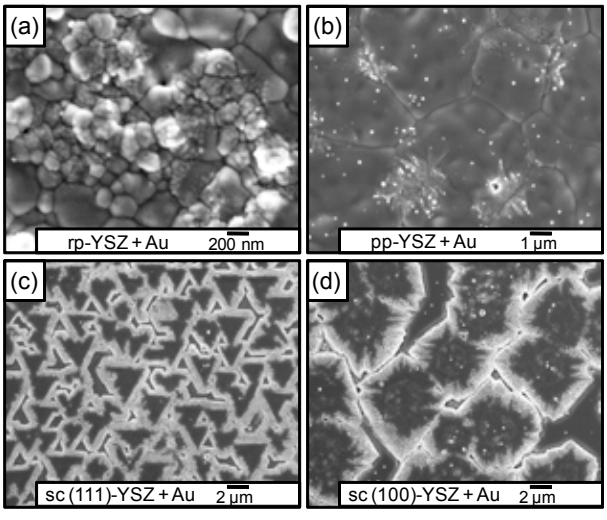

Fig. 1. Crystallization of 5 nm-Au colloids on (a) rp-, (b) pp- and (c, d) sc-YSZ ((111) and (100), respectively) plates, after annealing at 1000°C for 2 h.

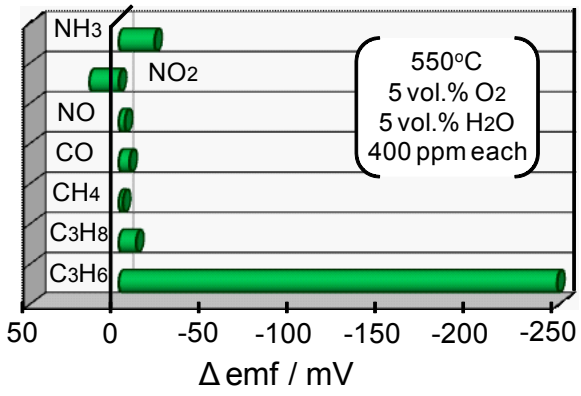

Fig. 2. Cross sensitivities to various gases (400 ppm each) at 550°C under the wet (5 vol.% H_2O) for the sensor based on rp-YSZ treated with 5 nm-Au.

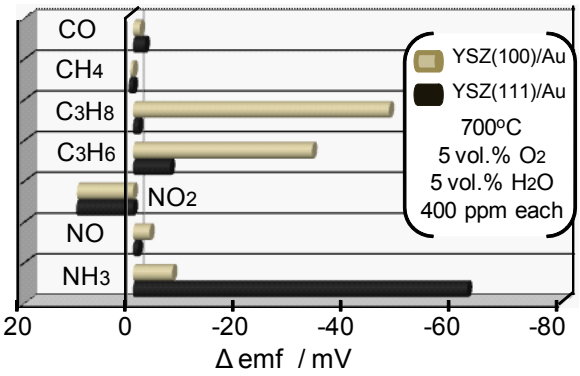

Fig. 3. Comparison of the cross sensitivities to various gases (400 ppm each) at 700°C under the wet condition for the sensors based on each of sc-YSZs attached with Au-SE.

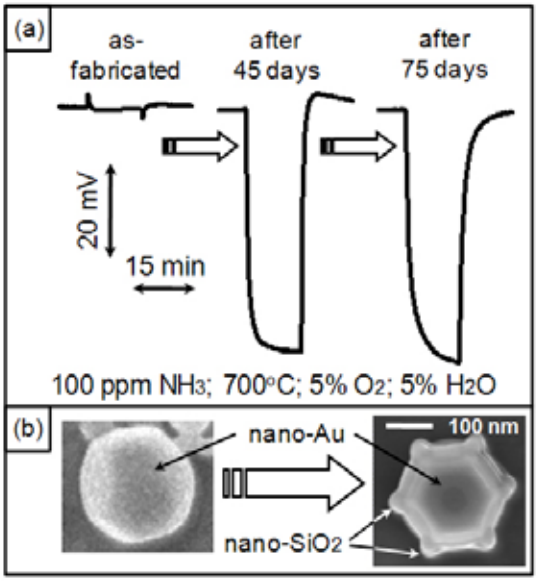

Fig. 4. (a) Response transients to 100 ppm NH_3 at 700°C under the wet condition for the sensor based on pp-YSZ treated with 5 nm-Au; (b) change of the shape of spherical Au particles to hexagonal-like Au-SiO_2 composite.

the help of adsorbed oxygen[3].

In the case of sc-YSZ plates, the gold followed the crystalline orientation of YSZ and formed the conductive (100)- and (111)- oriented Au domains with square- and triangular-like geometry, respectively (Fig. 1, c and d). As a result, the sensor based on YSZ(100) with Au-SE exhibited high but not selective responses to HCs at 700°C, whereas the sensor based on YSZ(111) gave selective and sensitive response to NH_3. Such a discrepancy in the sensing characteristics can be attributed to the dissimilar affinity and catalytic activity of variously-oriented Au domains to different gases.

The morphology of pp-YSZ can be considered as an intermediate between rp- and sc-YSZ plates. So, only partial Au clustering was found along the grain-boundaries and considerable amount of Au nano-particles were observed on the YSZ surface (Fig. 1, b). The as-fabricated pp-YSZ-based sensor using Au-SE did not show attractive sensing characteristics. However, after 45 days of operation at 700°C, the present sensor was found to give sensitive and selective response to NH_3 and the NH_3 response was not altered even after 75 days of operation (Fig. 4, a). SEM and EDX analyses revealed a gradual accumulation of nano-SiO_2 impurities on the surface of nano-Au particles (Fig. 4, b) changing their shape from spherical to hexagonal. In turn, it might result in change of its catalytic activity to gas-phase oxidation because some of active Au clusters are hidden by SiO_2. Additionally, high NH_3 sensitivity can be promoted by possible acid-basic interaction where acidic SiO_2 nano-particles catch and bind basic NH_3 gas molecules.

Thus, based on the obtained results, we are currently designing and constructing the high- performance YSZ-based sensor using nano-structured SEs for the selective and sensitive detection of carbon monoxide.

References

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