INFLUENCE OF SEMICONDUCTOR METAL OXIDE PROPERTIES ON HIGH-TEMPERATURE GAS SENSING CHARACTERISTICS

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Semiconductor metal oxides (SMOx) are widely used in gas sensors due to their excellent sensing properties, abundance and ease of manufacture. The best examples of these sensing materials are SnO_2 and TiO_2 that have wide bandgap and offer unique set of functional properties, the most important of which are electrical conductivity and high surface reactivity. The main material specific aspects that strongly affect the gas sensing properties and can be controlled by synthesis method are morphology/nano-structuring and dopants to vary crystallographic structure of metal oxide sensing material.

High temperature gas sensors are mainly designed to solve gas detection and monitoring problems with high operating temperature environment such as gas turbines, combustion system of power plants and for control of engine emission, exhaust gas monitoring and environmental protection. Such sensors have to operate with reasonable sensitivity under harsh conditions such as high temperatures in coexistence of multiple gases and high humidity. Good sensing properties are difficult to achieve under high temperatures gas environment by using simple semiconducting metal oxides. Therefore the development of innovative sensor materials is required for achievement of excellent high temperature sensing performance towards NOx. Literature focuses on cost effective metal oxide based gas sensors operate mostly at temperatures <400°C with only a few exceptions above 400°C. High-temperature NOx-sensing is an increasing requirement for process. TiO_2 is one of the semiconducting oxides that are capable of operating at and above 600°C. However, TiO_2 is a high resistive n-type semiconductor with relatively poor conductivity for sensing oxidative gases such as NO_2. This disadvantage can be prevailed through addition of low valence dopants to alter its electronic structure. Another strategy is to use catalytically doped perovskite based titanium compounds such as $BaTiO_3$. Additionally, the sensor designs can be optimized, for instance memrister sensors with TiO_2 layers are reported to yield promising results.

This context reports the sensor material developments achieved as resistive sensors using doped TiO_2 and Ti-compounds such as Rh-doped $BaTiO_3$. For the synthesis of doped TiO_2 layers, PVD-Sputtering process was utilized, while Rh-doped $BaTiO_3$ was synthesized by co-precipitation method. Doping of TiO_2 through trivalent cations promotes p-type behaviour exhibiting good sensing properties to NO_2 at temperatures above 500°C while Ni-doping displays the maintenance of n-type behaviour and better H_2-sensing properties at 600°C. Sensor design plays also role in sensors properties by using the same sensor material. Thus, the application of memrister sensor design with undoped and Cr-doped TiO_2 reveals that the sensor operation temperature can be decreased significantly, as the sensitivity increases a factor of 10-25. Thus, NO_2 sensing can be achieved already at 120°C with a very high sensor signal (almost 25 times higher that of the one obtained with interdigital gas sensor design). On the other hand, nanoparticles of Rh-doped $BaTiO_3$ prepared as sensing layers of interdigital gas sensors show excellent NO sensing properties even at 900°C.