Material design based on wet process for highly sensitive semiconductor gas sensors

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Resistive gas sensors using semiconducting oxides have been proven to be well suited for detecting inflammable or oxidative gases from their advantageous features in sensitivity, stability, robustness and so on. The sensing body (resistor) used in sensors of this kind is a porous assembly of fine crystalline grains of metal oxide. The gas sensing phenomenon can basically be reduced into a combination of three basic factors, i.e., receptor function (surface properties), transducer function (inter-grain properties) and utility (kinetic factor determined by diffusion and surface reaction).

Receptor function concerns the ability of the oxide surface to interact with the target gas. If the sensor is made of a neat oxide, the surface oxygen, especially adsorbed oxygen, of the oxide acts as a receptor. In air, oxygen is adsorbed on the oxide grains as negatively charged ions, inducing a surface space charge layer depletive of electrons or increasing the work function of grains. Upon exposure to the target gas, the adsorbed oxygen is consumed and decreased down to a steady state level, resulting in a corresponding decrease in work function. When the surface is loaded with a foreign receptor like PdO, it acts as a receptor stronger than the adsorbed oxygen, eventually giving rise to a far larger decrease in work function upon exposure to the gas.

Transducer function concerns the ability to convert the change in the work function of grains into a change in electrical resistance. Many years ago, Yamaoze et. al. focused first attention on the size effect. As found with neat SnO_2 devices, electric resistances in air as well as those under exposure to H_2 diluted in air, began to increase sharply when the size of component SnO_2 grains decreased beyond a critical point (about 6 nm in diameter). Recently we succeeded in deriving a theory for the response of a neat semiconductor sensor to oxidizing as well as reducing gases. The theory for grain size effect has been reconstructed by combining the electronic equilibrium inside each component crystal with the chemical equilibrium or steady state of surface reactions taking place outside and formulated for sensor devices using thick plates of semiconductor.

In the above, no attention has been paid on the location of the oxide grains in the sensing body. The target gas molecules diffuse into the sensing body while reacting with the oxide surface. If reaction rate is too large compared with diffusion, gas molecules are mostly consumed in the shallow region of the sensing body and can not reach the grains located at inner sites, leaving them unutilized for gas sensing and thus resulting in a loss in sensor response. How to elaborate the sensing body to have microstructure favorable for gas diffusion holds a key to improving the sensor response.

To obtain the high performance of the semiconductor gas sensors, we think that the combination of the above three basic factors is most important. In addition, wet processing seems to be suitable for material design based on the above basic factors. We believe that wet preparation methods including colloidal processing are worthy of being exploited thoroughly for this purpose. In this presentation, I show the some wet methods, for examples, the preparation of SnO_2 cluster sols by hydrothermal treatment for improvement of gas diffusion, the colloidal particle of SnO_2 loaded with foreign metal like Pd for surface modification and so on.