Effect of thickness on H₂ gas sensitivity of SnO₂
nanoparticle-based thick film resistors

S. G. ANSARI, P. BOROOJERDIAN, S. K. KULKARNI, S. R. SAINKAR¹,
R. N. KAREKAR, R. C. AIYER
Centre for Advanced Studies in Material Science and Solid-State Physics, Department of
Physics, University of Pune, Pune 411007, India
¹ National Chemical Laboratory, Pashan Road, Pune 411008, India

The effect of thickness on the p.p.m. level H₂ gas sensitivity of SnO₂ nanoparticle-based thick
film resistors is reported. The nanoparticles are synthesized by a sol-gel method and the
films are prepared using standard screen printing technology. The thickness of the films is
varied from a few micrometers to a few hundred micrometers. The results indicate that the
sample having thickness 76 μm gives the maximum sensitivity. The mechanism of the
change in sensitivity with thickness is discussed.

1. Introduction
The use of resistive, adsorption-based sensors has been increasing over the past few years for purposes
such as detection of smoke, oxidizing or reducing gases (O₂, CO, CH₄, CO₂, etc.) and humidity [1-4].
A variety of materials have been used for gas sensing, including ceramics that often consist of a combination
of metal oxides. SnO₂ is one of the semiconducting materials very widely used for sensing oxidizing/re-
ducing gases due to its high sensitivity to small concentrations of gas (at p.p.m. level). These sensors are
not able to differentiate the gases in a mixture, so selectivity is a serious problem. There are [4] several
ways of improving the selectivity of gas sensors. The commonly used methods are (1) temperature control
(2) catalysts on the surface of sensing elements and (3) thickness variation.

The temperature effect is due to the reaction be-
tween hydrocarbon and oxygen. For hydrocarbon
molecules (RH₂) adsorbed on the sensor surface, the reaction be-
tween the hydrocarbon molecules and the
surface oxygen is

\[ \text{RH}_2 + 2\text{O}^- \rightarrow \text{RO} + \text{H}_2\text{O} + 2\text{e}^- \]

The rate of this reaction is a function of temperature.
When the sensor is operated at low temperatures, the
reaction is slow. When the sensor is operated at higher
temperatures, the reaction occurs so rapidly that the
sensor is not able to detect the combustion reaction.
Therefore, a maximum is exhibited on a sensitivity versus temperature curve. As the reaction rates for the
various gases are different, the maximum for each gas
occurs at different temperatures [4]. The catalyst on
the surface of the basic material acts as an intermedi-
ate layer, creating extra sites for adsorption. The
thickness dependence is because of the space charge
layer, which varies with thickness and oxygen
chemisorption [1-4]. The sensitivity variation is
caused by the variation in space charge. The space
charge is a function of the adsorption of the reactive
gases.

In general, these semiconductor sensors detect low
concentrations of gases and convert the gas concentra-
tions directly to the change in electrical conductance of the sensor material. With the aid of a simple electrical
circuit, a portable inexpensive solution is achieved.

For this work, nanoparticles of SnO₂ are syn-
thesized by a sol-gel method and are used in the form
of thick film along with the lead borosilicate glass for
better adhesion. We reported the H₂ gas-sensing prop-
erties of the films in an earlier paper [5]; it shows that
the use of nanoparticles increases the sensitivity of the
sensor by orders of magnitude and it gives a higher
value than previously reported by others [6-10]. In
this paper we will concern ourselves with the sensitiv-
ty of thick film resistors based on SnO₂ nanoparticle
gas sensors, mainly for H₂, with thickness variation
for 300 p.p.m. gas concentration.

2. Experimental procedure
SnO₂ nanoparticles were synthesized using a sol-gel
method. SnCl₂·5H₂O (AR grade) was dissolved in
distilled water to make a 0.1 M solution. The solution
of SnCl₂ and H₂O was mixed with ammonia
(NH₄OH, AR grade). The resulting precipitate was
washed thoroughly with distilled water many times to
remove excess ions (Cl⁻ and NH₄⁺). The resulting
milky-white gel was dried for 24 h at 100 °C. The dried
precipitate was ground into powder and passed
through a 200 mesh size. The resulting powder was
calcined for 4 h at different temperatures to obtain
SnO₂ of various sizes [5].

X-ray diffraction patterns of the calcined powder (at
500 °C), as synthesized by the above method, are
shown in Fig. 1. The particles have a crystalline nature
as indicated by the decrease in the diffraction peak
width, with diameter 25 nm.
Tin oxide occurs \[11\] in various phases: orthorhombic, tetragonal, cubic or triclinic. But here only the tetragonal phase was obtained.

X-ray diffraction analysis of tin oxide powder annealed at 500 °C, as well as powders made into thick films (suitable for resistors) was carried out using a Philips PW-1840 diffractometer. CuKα radiation (\(\lambda = 0.1542\) nm) was used as the X-ray source. Particle size analysis was made using the width of the diffraction line at 2θ = 52.2 and using the Debye-Scherrer formula

\[
D = \frac{0.9 \lambda}{B \cos \theta}
\]

where \(D\) is the diameter of the particles, \(\lambda\) is the X-ray wavelength and \(B\) is the full angular width of the diffraction peak at half the maximum for diffraction angle 2θ.

X-ray diffraction analysis using the above method gave the average particle size. Further information about the particle size and particle shapes was obtained by examining them under Leica-Cambridge Stereoscans S-440 scanning electron microscope. The samples were mounted on a standard specimen mounting stub and were coated with a thin layer of conductive gold (a few tens of nanometers) using a Polaron E5000 sputter coater to prevent charging of the specimen. The micrographs with 40 kV EHT and 25 pA beam current were recorded by a 35 mm camera attached with the high resolution recording unit.

Stannic oxide prepared by the above method was used as the basic material. SnO₂ paste was prepared with 15% of lead borosilicate glass frit as a permanent binder; ethyl cellulose and butyl carbetol acetate were added as temporary binder to get a thixotropic paste \[3\]. The paste was then printed on alumina substrate (5 mm × 10 mm), dried for 20 min then fired at 850 °C using induction heating. Silver electrodes were printed after firing the films. The film thickness, as measured by light section microscope (BK 70 × 50 Carl Zeiss, Jena) with an accuracy of 0.5 µm, varies from 29 to 210 µm. The d.c. resistance was measured by digital electrometer (Keithley EA-614).

The measurements of p.p.m. level gas sensing were carried out using a static measuring system. The d.c. resistance (gigaohms) of the sample was directly measured using an electrometer. Hydrogen gas (300 p.p.m.) was injected into the chamber, made easier because the chamber was slightly evacuated at the start. After injecting the gas, the electrical characteristics of the sample were investigated while changing the temperature. The gas sensitivity was calculated by taking the ratio of \(R_{\text{gas}}\) to \(R_{\text{air}}\). The samples were tested up to 250 °C from room temperature.

3. Results and discussion

Fig. 2 shows the high resolution SEM photograph of calcined powder at 500 °C. The particle size appears to be 100 nm; this is probably due to agglomeration or partial crystallization of the particles. If the particles were not completely crystallized then X-ray diffraction would estimate a smaller size.

Sensor elements were fabricated with SnO₂ nanoparticles calcined at 500 °C and with 15% of lead borosilicate glass frit, followed by firing at 850 °C. As can be seen from Fig. 3, even though the firing temperature and time were held constant in all these cases, the original particle size of SnO₂ nanoparticles affected the porosity of the resulting films.

Fig. 4 shows the X-ray diffraction pattern of the thick film in Fig. 3. The thick film mixture with lead...