



An Optimized Platinum (Pt) Doped Tin-oxide(SnO_2) Ink for Deposition of Gas Sensing Thick Film on LTCC Micro-hotplate

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Abstract

An optimized platinum (Pt) doped tin oxide (SnO_2) ink was prepared by chemical route and was deposited on low temperature co-fired ceramics (LTCC) micro-hotplate by screen printing. An alkoxide ink was prepared by mixing tin (II) 2-ethylexanoate (17 wt%) with isopropanol (27 wt%) and SnO_2 powder (55 wt%). Doping of the ink was done using Pt (1 wt%) which increased the resistance of SnO_2 film at room temperature and also reduced the operating temperature. The temperature of sensor was obtained and stabilised using MOSFET based temperature stability circuit. Film characterization was performed using Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) technique. Small grain size and high porosity is the requirement for good sensing. The grain size was found to be in the range of 150-180 nm and the film was sufficiently porous. Resistance change of the film was also investigated in the presence of carbon monoxide (CO) to assure gas sensing.



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Introduction

Elevated atmospheric pollution has raised the demand for effective and inexpensive system for detection and quantification of environmentally hazardous gases. The detecting systems available in market are mostly based on optical spectroscopy and gas chromatography which are both expensive

and time consuming analytical techniques. Gas sensors are promising alternatives for environmental measurements and those based on metal oxide semiconductors (MOS) are extensively used because of their low cost, high sensitivity, wide range target selectivity, short response time and long life¹. Sensing mechanism of such sensors is based on the

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redox reactions taking place at the grain boundaries of the film. MOS gas sensor materials, which are typically n-type semiconductors form an electron depleted surface layer under normal atmospheric conditions and a typical temperature range of 300-600°C. The atmospheric oxygen at such a high temperature adsorb on the surface and take out electrons from the film surface forming O^- and O_2^- species. Reducing gases (like CO, H_2) and oxidizing gases (like NO_2) react with the species and modulate the depletion layer thickness leading to measurable change in the resistance of the material². Among all sensors based on metal oxide semiconductors, the sensitivity of SnO_2 -based ones is relatively high, leading to its greater popularity³.

LTCC is a special material system manufactured by using green sheets made up of 40% filler (ceramics mainly alumina), 45% glass (SiO_2) and 15% organic vehicle and produced by tape casting⁴. LTCC is a favoured technology for preparing miniature integrated packages and devices for various sensor and actuator applications⁵. Gas sensors manufactured in LTCC technology show high temperature stability, possibility of integration and inexpensive manufacturing. LTCC can form small compact sensors with low power consumption due to their low thermal conductivity compared to standard devices on alumina. Optimum design of micro-hotplate can reduce power consumption significantly⁶.

Conventional SnO_2 inks consist of glass as binder which decreases the conductivity of the film^{7,8}. J.P. Viricelle et al. proposed a solution for the problem by developing a new ink which had no glass and

was developed by adding SnO_2 powder to tin oxide gel. Due to less adhesion and more complexity in preparation of the ink, another ink was prepared with tin alkoxide. Platinum (Pt) doping can promote sensor response to CO gas. During thermal treatment, more oxygen molecules gets adsorbed onto the SnO_2 film surface when doped with Pt as it forms the adsorption site for dissociation of O_2 to O^- and O_2^- species⁹. This attracts more CO towards the oxygen species and release CO_2 , thus increasing the sensitivity with faster response time. Pt also lowers the operating temperature required for sensing CO¹⁰. So, investigations presented in this paper concern with the addition of Pt to the tin alkoxide ink.

Experimental Details

Temperature Stability Circuit

Sensitivity of a gas sensor depends on the working temperature, which can be realised using a hot-plate. For most MOS gas sensors, high operating temperature is required due to reaction temperature of O^- . The sensitive layer has to be preheated to an elevated temperature so as to increase the probability of gas molecule adsorption and promote the consumption of ions of the sensing material. With the consumption of ions, sensing film conductivity increases realizing the sensing function. To maintain the sensing film at a desired temperature, temperature stability circuit was simulated in PROTEUS 8 professional and designed on LTCC substrate. Block diagram is shown in figure 1.

Fabrication of Micro-Hotplate

For an optimized gas sensor design, low power consumption and lower heat losses due to conduction, convection and radiation by the heater

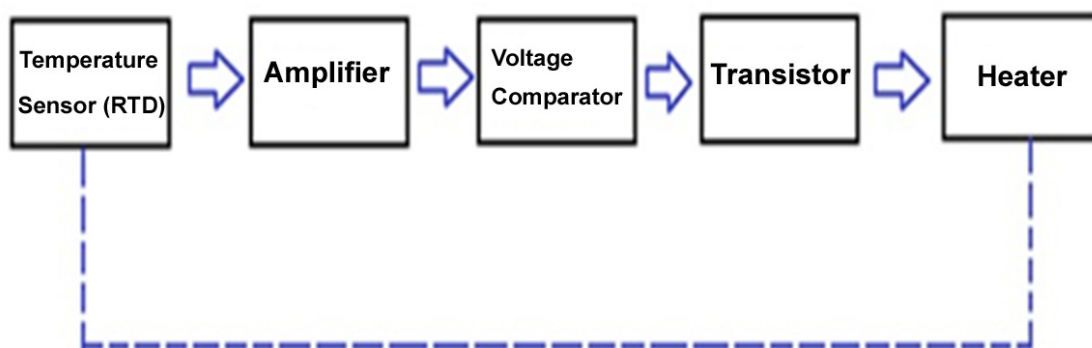


Figure 1: Block diagram of Temperature Stability circuit

is required². Heater shape and size should be such that the heat is uniformly distributed and less power is consumed. These days micro-hotplates are designed for the heating of the sensing film on it. LTCC having low thermal conductivity, is appropriate for low heat loss micro-hotplate. LTCC micro-hotplate as shown in figure 3, was designed having size 3mm x 3mm consisting 3 layers of fired green tapes with top side printed with gold electrode in a specific design (via-butterfly as shown in figure 2) and the rear side printed with platinum as heater. Sensing film was deposited on the top of electrodes.



Fig. 2: Via-Butterfly LTCC Microhotplate

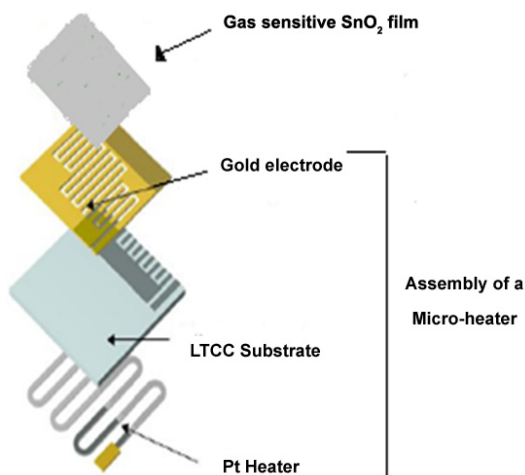


Fig. 3: Schematic diagram showing the assembly of a micro-hotplate (micro-heater) with the deposited SnO_2 film. Electrode was screen printed on the top of LTCC substrate (3mm x 3mm) in a specific pattern and the heater on the rear side. Film was deposited on the electrode (leaving the testing pads idle) by screen printing technique (using 200 mesh mask suitably covered to get the desired layout of the film).

It was operated between the temperature range of 25-250°C. Maximum operating temperature was 450°C. At around 3V, it produced a temperature of 250°C with power consumption of 1W. This design of LTCC micro-hotplate had power consumption less than thick film micro-hotplate (~2.5 W) but more than Si micro-hotplate (~0.02W) in line with the data given in¹².

Development of Ink

Tin(II) 2-ethylexanoate was used to develop the tin alkoxide ink because it does not produce impurities

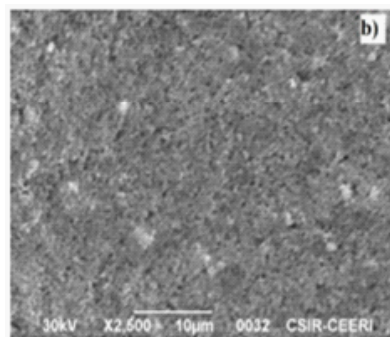
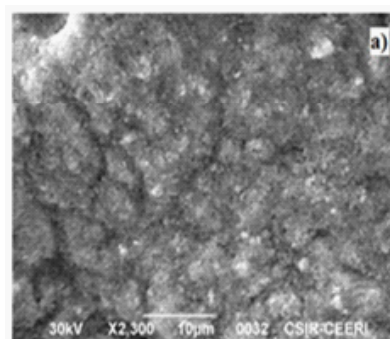


Fig. 4: SEM micrograph of the deposited film

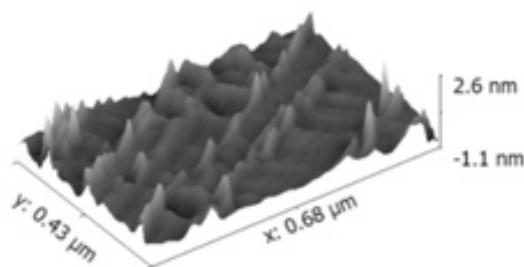


Fig. 5: Three dimensional AFM image of SnO_2 film.

like Cl, Na, etc. which might modify the conductivity of the film⁷. Isopropanol (27 wt%) was added to tin(II) 2-ethylexanoate (17 wt%) and was stirred. After sometime, SnO_2 powder (55 wt%) was added and the stirring was continued. After 2 hrs, the developed alkoxide ink was doped with Pt (1wt%) and again stirred for 1 hr. All SnO_2 granules of the powder were crushed and well-mixed. The ink was sufficiently viscous suitable for screen printing.

Ink Deposition

Screen-printing technology was used to deposit the ink on LTCC micro-hotplate as it is a low cost production process that enables to deposit sensing elements for gas sensors, mainly on ceramics. Using

computer aided screen printing, micro fabrication is possible with good resolution.

The ink was deposited using 200 mesh mask. After deposition the film was kept at room temperature for 20-30 min so that it stabilizes. Then it was dried at 150°C for 30 min and then annealing was done at 600°C profile for approximately 2hrs under ambient air.

Results and Discussion

Film Characterization

Surface morphology of the film was studied by SEM. Figure 4(b) shows the SEM micrograph of the deposited film. Figure 4(a) is the zoomed SEM

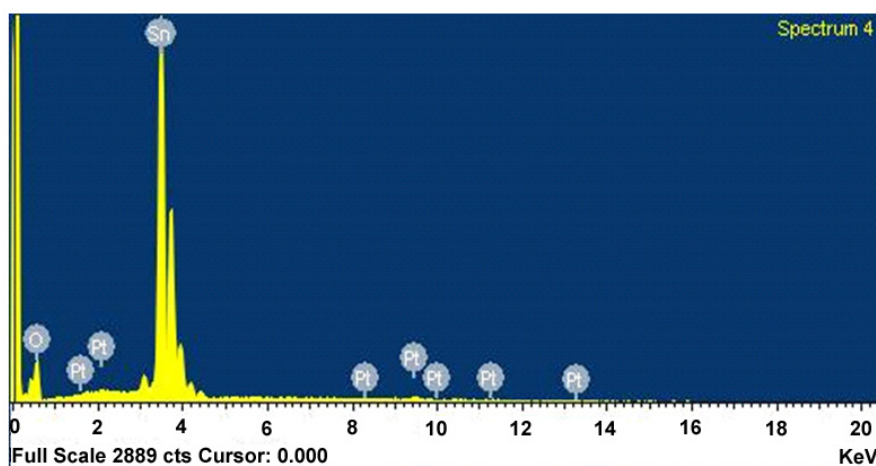


Fig. 6: EDX analysis spectra of Pt-doped SnO thick film annealed at 600°C profile

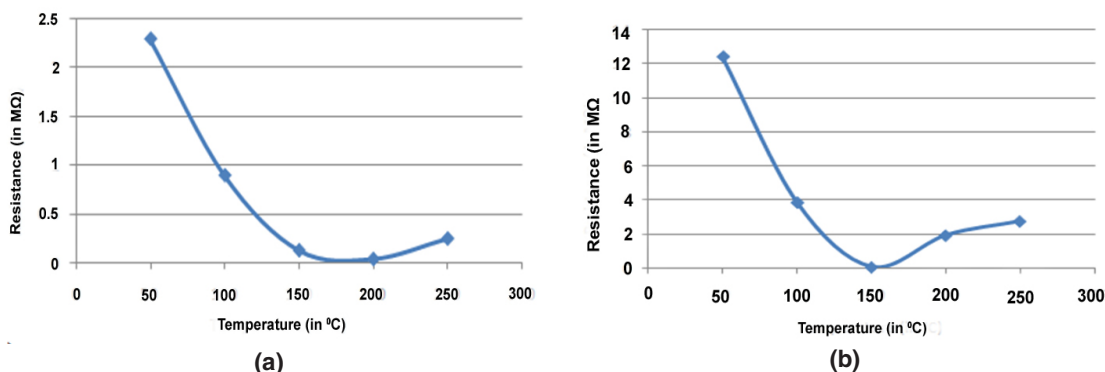


Fig. 7: Variation of resistance with temperature in 50ppm CO gas of (a) alkoxide ink film (b) alkoxide ink with Pt doping film

image of the film to visualize the grain size and porosity. The grain size was found to be in the range of 150-180 nm.

Thickness of the film was measured using Stylus profiler DEKTAK 6M and was found to be around 39 μm .

The Minus K Technology system by Digital Instruments was employed for the AFM experiments. The tapping mode was used for the morphology characterization so as to protect the AFM tip from the rough surface of the film. The three dimensional AFM image of SnO_2 film shown in figure 5 has a measured surface roughness of (Area Ra 1.94 nm) and (Area RMS 2.75 nm) which shows well separated slightly conical nano columnar structure and reveals that the film was sufficiently porous with large surface area.

EDX analysis was done to confirm-

- Composition of screen printed film
- Atomic and wt% of deposited material

It is an approximate analysis which showed the presence of Sn and O and small amount of Pt. Figure 6 illustrates that no other impurity elements were found (also shown in table 1).

Electrical Characterization

Table 1: Quantitative elemental analysis

Sample- SnO_2	Weight %	Atomic%
O K	37.71	68.28
Sn L	60.94	31.45
Pt L	1.35	0.27
Total	100	100

Figure 7 shows the variation in resistance of the deposited film with temperature in presence of 50 ppm CO gas. At room temperature no significant drop was noticed. As the film was heated in CO atmosphere, the resistance started falling considerably. The film on exposure to CO shows more fall of resistance than the film not exposed

to CO. This may be due to the fact that on heating a semiconductor film, electrons generated are taken up by ambient oxygen and only a few are left for conduction where as heating the film in CO atmosphere releases those taken up electrons by oxygen, thus increasing the electron concentration and reducing the resistance significantly. Above a critical temperature, the resistance of the film exposed to CO gas started increasing which may be due to the fact that the added desorption due to the target gases is small relative to the steady-state desorption in air¹¹.

On comparing films deposited using alkoxide ink and alkoxide ink with Pt-doping at room temperature, increased resistance was found in the later. Moreover, Pt reduced the operating temperature, because it acts as a catalyst speeding up the adsorption of oxygen and dissociation into oxygen species, which leads to more CO interaction with the species, thereby reducing the operating temperature to detect the same concentration of CO.

Conclusions

It was found that the film developed and printed on LTCC had good adhesion and showed high sensitivity under low operating temperature due to the presence of Pt compared to conventional inks. This paper also attests to the fact that LTCC can become a major substrate for gas sensors in coming years over alumina because it can produce gas sensor in an integrated package in a small area with minimal power consumption, if properly exploited. Development of the film material using different concentrations of alkoxide ink, Pt doping and use of SnO_2 nano powder in place of SnO_2 powder can be further investigated.

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