Perovskite structure pristine and palladium-doped bismuth ferrite for nitrogen dioxide gas sensor

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**1 Pd- doped Ferrite**

The pure BFO has demonstrated the less selectivity and sensitivity towards various gases. Therefore, the development of a synthesis method for effectively enhanced the sensitivity and selectivity is urgently required. Recently, the dopant effect of nobel-metals such as Pd, Au, Pt and Ag have been widely investigated to the synthesis of sensing materials. Mulla et al. reported that Pd doping in magnesium ferrite enhance the sensitivity toward LPG gas and lowering the optimum operating temperature as compare with pure magnesium ferrite(Darshane and Mulla, 2010). Bhagwat el al. investigated that Pd-incorporated in nickel ferrite thin films reduced in operating temperature and faster the response rate towards the chlorine gas (Rao et al., 2016a). Bhagwat el al. successfully synthesized Pd- doped in nickel ferrite and investigated in their sensitivity towards various organic volatile gases (Rao et al., 2016b). Li et al. reveal that Ag modified bismuth ferrite nanosphere not only enhance the density of hole and amount of gas adsorption but also has a catalytic effect on chlorine-based gas sensor performance (Li et al., 2018). All the above indicated that nobel-metal doping is regarded as a good way to enhance the sensitivity and selectivity of gas sensor.

**2. Experimental section**

***2.1 synthesis of BFo and Pd-BFO***

The all chemicals including bismuth nitrate pentahydrate [Bi(NO3)3·5H2O], ferric nitrate hydrate [Fe(NO3)3·9H2O], citric acid [C6H8O7], diluted nitric acid (20%HNO3), ammonium hydroxideand palladium (Pd) were purchased from the Sigma-Aldrich and were used as received without any purification. Briefly, 0.1 mole of Bi(NO3)3·5H2O[3 ml diluted nitric acid (20%HNO3) and 47 ml waterwere used for dissolving Bi(NO3)3·5H2O], 0.1 mole of Fe(NO3)3·9H2O and 0.1 mole of citric acid [C6H8O7], considered as the chelating agent were dissolved in 50 ml double-distilled water. The prepared solutions were transferred and well mixed in a glass beaker with 250 ml capacity, called as A-solution. The pH~10 of the A-solution was maintained by drop-wise addition of ammonium hydroxide solution and final solution was called B-solution. Finally, B-solution was kept on magnetic stirrer with hot-plate instrument and maintained at 100 °C temperature for evaporating water molecules and transform it to a gel. After ~5 h constant heating process total waters molecules evaporate to form a thick dry gel which automatically ignited and ash was remained in the beaker. The obtained powder was transferred in crucible and annealed in muffle furnace at 500°C for 4 h to remove residual impurities. Finally, brownish powder (BFO) was obtained. The brownish powder of BFO was grinded well in mortal-piston before making thick films onto non-conducting glass substrate (single layer of scotch TM tape, 1µm and total 1 cm2 active area), these thick films called as pristine BFO films. In the next step, pristine BFO thick film was surface treatment with Pd solution [as considered one of the good catalytic material], these thick films called as Pd-BFO. Furthermore, the BFO films were characterized by various characterization techniques and finally were envisaged for gas sensing applications.

***2.2 Characterization details***

The X-ray power diffraction pattern of the as prepared pristine BFO and Pd-BFO film sensors were carried out to identify the crystalline phase by using Rigaku D/max- γ B X-ray diffractometer with Cu Kα radiation sources (λ=1.5418 Å). The Field-emission scanning electron microscopy (FE-SEM) images were obtained to determine surface morphology at various magnification of both sensors separately. Moreover, the surface elements were from Energy dispersive X-ray analysis (EDAX). The Beuauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) measurement were performance by using N2 adsorption-desorption at 77 K for knowing surface area and pore size distribution of both sensors.

***2.3 Sensor measurements***

The gas sensitivity of the pristine BFO and Pd-BFO thick film sensor was measured using a computer-aided setup. Briefly, the gas sensor set-up was containing a 250 ml cylindrical stainless-steel vacuum chamber. The digital display PID controller incorporated in vacuum chamber to set desired temperature range. The voltage stabilizer is utilized to protect voltage variation during operational process. The presence of different concentration of gas, the change in resistance with respective time was measure by using computer controlled six-digit Keithley 6514 electrometer. A Keithley electrometer was connected to computer device *via* RS 232 interface cable to note the variation in resistance of gas. The various target gases of 1000 ppm concentration capacity obtained from Cryo gases Pvt. Ltd., Mumbai, India were used. The gas sensitivity of film was calculated by using eq. 1 [39].

(1)

whereas, Ra is the resistance of sensor in presence of air and Rg is that upon exposure of NO2 target gas

**Reference**

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