BOITUMELO MAFALO MABAKACHABA

PROJECT: Investigation and development of 1-dimension VO_2 nano-sensor which exhibit high detection capabilities for hydrogen gas at ambient temperature.

Investigation and development of Vanadium dioxide(VO_2) based room temperature hydrogen(H_2) gas nano-sensors.

Background and Rationale

In 2019, almost 92 million motor vehicles were produced worldwide (In South Africa, more than half a million automobiles annually of all types). In line with Climate change regulations & the reduction of the CO_2 footprint, Hydrogen (H_2)-generated energy has gained a sound momentum in the transportation sector especially. Indeed, energy storage and increasing number of direct applications of H2 as powered cars or fuels cells are highly demanded due to the discontinuity of primary energy produced from renewable sources of energy like sun power or wind. Several governments and researchers around the world, due to the global awareness greenhouse gas emission, air pollution and energy security issues were led to develop secure and environmentally friendly fuel systems which must be switched gradually to clean, affordable and reliable energy reaching the global drivers for a sustainable vision of the future energy market. Among versatile alternative energy sources, hydrogen (H2) is one of the attractive solutions to succeed the current carbon- based energy system. H_2 represents the cleanest and low zero emission energy vector for transport application. In addition, it is the most abundant element on earth with the highest specific energy content with 141.79 MJ/kg. The high risk of explosions while handling hydrogen has led to increased efforts around improving on the safe storage and usage of hydrogen [1; 2].

In relation to the hydrogen economy in general, and hydrogen gas sensing, and in addition to standard nano-powders/thin films structures, extensive set of novel nano-scaled oxide materials such as nanowires, nanotubes, nanorods, and nanobelts based systems are being investigated as ideal candidates for gas sensing applications. This is due to their set of singular surface characteristics, shape anisotropy and readiness for integrated devices [3; 4; 5; 6; 7]. This latter component includes their large surface/volume ratio, single crystalline structure due to their preferential growth, and great availability of surface-bound chemical active sites [8; 9]. As previously reported, the nanostructures of well-established gas sensing materials such as SnO_2 [10; 11; 12], ZnO [13; 14]. In_2O_3 [15; 16], and WO_3 [17; 18] have shown higher sensitivity and selectivity, quicker response, and faster time recovery, as well as an enhanced capability to detect gases at low concentrations compared with the corresponding thin film materials [19; 20]. While the overall sensing characteristics of these so called 1-D nanomaterials are optimal, they are efficient at high temperature; generally, above 200 C, resulting in significant power consumption, in addition to complexities in device integration, which limits their technological applications. Consequentially, there is still space and need to develop 1-D nanomaterials for gas sensors that have very good sensing performance but at room temperature. Unfortunately, for room temperature applications, there is a necessity to dope the above-mentioned nano-scaled oxides with high-cost noble metals such as Pt, Pd, Au, and Ru. Indeed, as demonstrated by Tien et al. and Wang et al. [20; 21], ZnO nano-rod sensors showed higher H_2 sensitivity and quicker response at room temperature for ZnO nano-rods surface- modified by sputter-deposited clusters of Pd or Pt when compared with the undoped and corresponding thin film sensors. Ramgir et al. [22] reported that 0.48 wt% Ru-doped SnO_2 nanowires exhibited the highest sensitivity towards NO_2 gas at room temperature while Neri et al. [23] reported that Pt-doped In_2O_3 nano-powders showed better gas sensing performances to oxygen at room temperature compared with the un-doped samples. In 2014, Maaza et al reported, for the first time [24], an unexpected room temperature enhanced H_2 sensing property for a specific phase of vanadium dioxide

Objectives and methodology

The experiment for the synthesis of VO2 nanostructure like nanorods (NRs) and nanocolliods (NPs) were conducted at iThemba LABS, material research division via hydrothermal method. Firstly, the source (V2O5) was reduced using Oxalic acid, the mixture was stirred using magnetic stirrer at elevated temperature to reduce the reaction time and annealed at 500 ◦C for 2 hours to obtain the required the preferred phase of VO2. Seven measurement techniques were applied to examine the VO2 nanostructures. Scanning electron microscopy (SEM) and Transmission electron microscopy were used to examine the morphologies of the VO2 nanostructures. Energy-dispersive X-ray spectroscopy in SEM was used examine the element information of the VO2 nanostructures as well. X-ray diffraction (XRD) examined the crystal type of the VO2 nanostructures. Photoluminescence spectroscopy was applied to examine the defects near the surface of VO2 NRs/nanobelts. X-ray photoelectron spectroscopy (XPS) was applied to examine the surface chemical information of VO2 systems and the standard in-situ two contact point -based system was utilized comprising a digital meter, analog meter, a graphic recorder, and data logger. The chamber consists of heating stage were the resultant VO2 nanomaterials on ITO and porous alumina substrate are placed and heated at temperature ranging from 25 ◦C - 170°C. The responses of resistance of VO2 nanostructures at different concentrations of H2 fluxes were measured upon injection of target gas balanced with Nitrogen (N2) as a gas carrier and refluxing with pure N2. The reproducible experiment was conducted with different H2 partial pressures carried by N2. More of the effective interaction between H2 and nanomaterials and high gas sensing response were obtained from high concentrations of O^- ions of the surface, where the additional defects on the nanomaterial quantified through lattice interspacing distance as a result of oxygen vacancies can act as absorption site for gas species which plays a urge role on the behaviors of metal oxide surface and reversibility of sensor characterization. Gas sensing selectivity, sensitivity, repeatability measurements and optimal temperature studies for gases such as Benzene, NO_2, CO_2, CH_4, SO_2, CO, H_2S and H_2 were conducted using KINESISTEC testing system at CSIR.

Timeline

Workpackage-1: Year 1/ Month1-3:

•Literature survey & the state of the art on gas sensing integrated technologies,

Workpackage-2: Year 1/ Month4-10:

•Synthesis, characterization & optimization of 1-D VO_2 pellets.

Workpackage-3: Year 2/ Month11-12:

•H2 Gas sensing studies onto optimized integrated interdigitated 1-D VO_2 onto glass, Al_2O_3 ceramic plates and silicon/SiO_2 substrate.

Workpackage-4: Year 2/ Month4-10:

- Synthesis, characterization & optimization of colloidal VO_2 to be embedded in porous Al_2O_3 substrate.

Workpackage-5: Year 2/ Month11-12:

- H_2 Gas sensing studies onto optimized integrated interdigitated colloidal VO_2 embedded devices.

Workpackage-6: Year 3/ Month1-12:

- Laboratory prototyping of flexible & tubular VO_2 H_2 gas sensors & life time cycling
- Participation in local & international conferences
- Chapter writing & Publications finalization and potential patent submission
- Final PhD dissertation draft

Results or preliminary data

i. Structural and Morphological analysis

VO_2 (M1) 1D nanobelts were successfully synthesized via hydrothermal process as observed in Fig. 1 below from the XRD and SEM analytical technique.

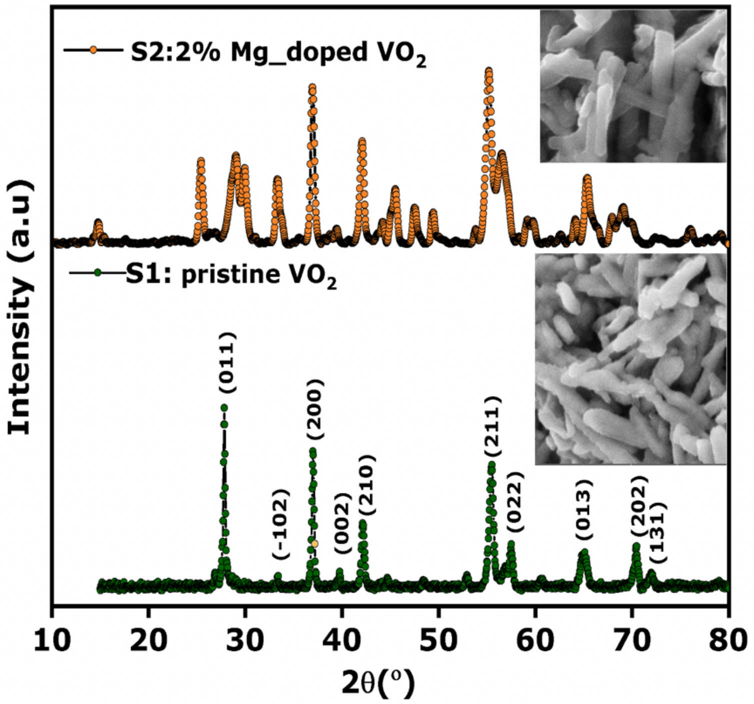

FIGURE 1: Structural and morphological analysis from XRD and SEM

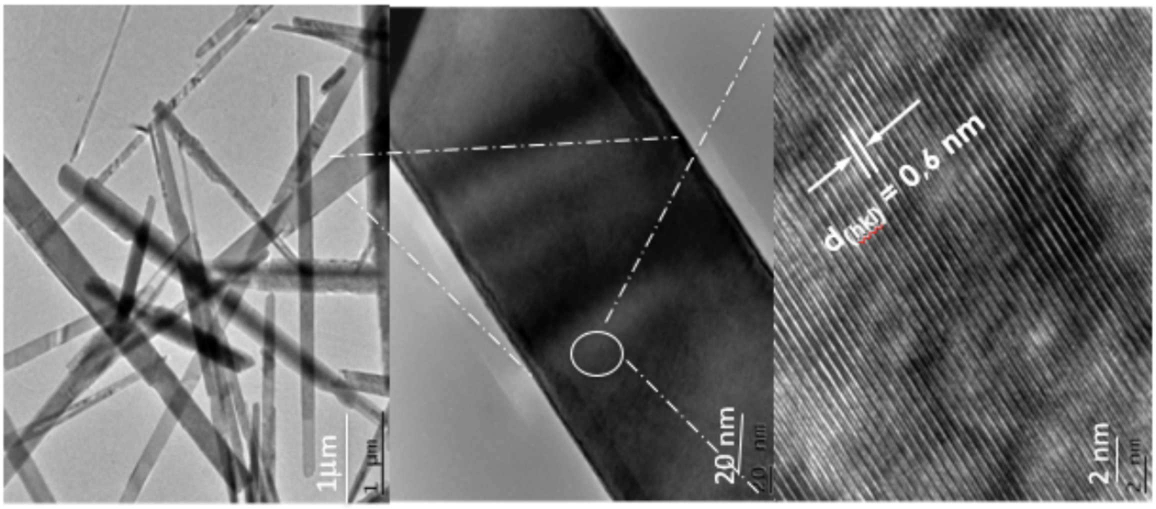

FIGURE 2: Morphological analysis from HRTEM

In Fig. 2, the filtered synthetic powder's electron transmission microscopy is displayed. Nanoparticles have a morphology like a nanobelt and display crystal-clear structural anisotropy. They have an average transverse size of 20–150 nm, a length greater than 20 m, and a thickness of less than 10 nm, according to a statistical imaging research.

ii. Gas sensing Analysis

- Preliminary Analysis for Hydrogen gas sensing

The gas sensing response for pure VO_2 nanostructures can be observed to grow as the injected gas concentration rises up to 90 ppm before decreasing at higher concentrations. (See fig.3) One significant benefit of VO2 nanobelts is that the sensor may be utilized at room temperature and has a detection limit of less than 14 ppm. It can also detect high concentrations of H2. The sensor has response and recovery times which are, respectively, between 850 and 1000 seconds and 450 and 700 seconds.

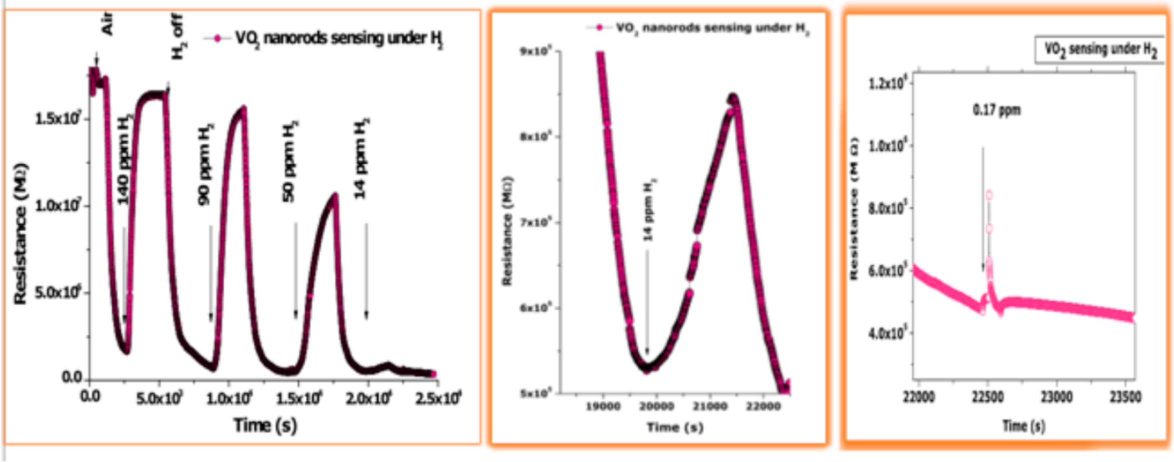

FIGURE 3: Sensitivity analysis for hydrogen gas experiment at room temperature.

- Preliminary Analysis for Nitrogen dioxide gas sensing

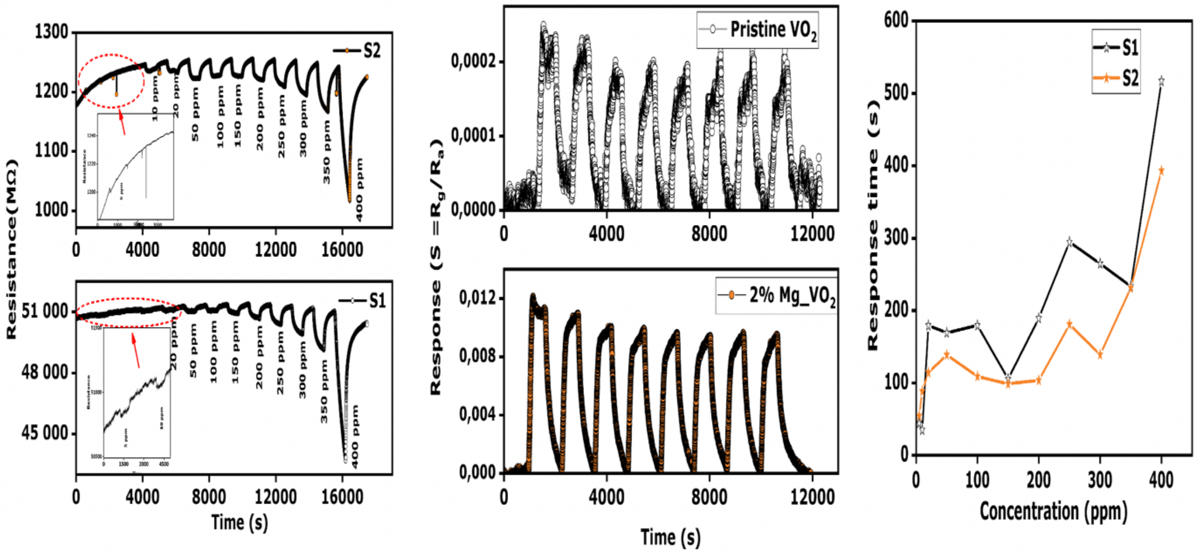

FIGURE 4: Sensitivity, Stability, and response time analysis for NO_2 gas experiment at room temperature.

In this case, pure and Mg-doped VO_2 NO_2 gas analysis were carried out to investigate sensitivity, stability, and response time for before and after doping VO_2 nano-sensors. Fig.4 the sensitivity measurements were carried out for NO_2 concentration ranging from 400 ppm to the lowest concentration approximately 5 ppm. The sensors exhibit good response and stability at show in the middle diagram for about 8 cycles. Mg impurities or dopants decrease the response time of the sensor, and this is very advantages because the sensor with detect the NO_2 quicker than the pure sensor.

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