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Oxygen Sensing Characteristics of Milled Metal Oxide Materials

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Abstract: Metal oxide materials are widely used as sensing material. Experimental studies have been conducted to explore the potential of fine metal oxide powders obtained by stirred bead milling for sensing of oxygen towards the thin film technique. Though the results indicate the potential of these materials for sensing, further optimization with respect to milling parameters and pelletizing are required to develop these as sensor materials.

Key words: Silica, titanium dioxide, stirred bead milling, sensing, oxygen

INTRODUCTION

Gas sensing is an important application in various industrial and war environments (Kannan *et al*., 2010). Several attempts have been made in literature towards development of efficient strategies for detection of gases with improved selectivity, sensitivity and time of detection (Sivalingam *et al*., 2011a; Hauffe and Vierk, 1950). Metal oxides are one of the widely investigated materials for gas sensing applications (Trinh *et al*., 2011). The method of preparation of a material influences the size, shape and hence the morphology and surface area of particles (Liu *et al*., 2006; Sivalingam *et al*., 2011a; Trinh *et al*., 2011; Lu *et al*., 2010). Sensing, being a phenomenon depending on the interaction between analyte and sensor material, is sensitive to surface area. The presence of grain boundaries improves surface area (Sivalingam *et al*., 2011b; Logothetis and Kaiser, 1983). Hence, the materials that are prepared by mechanical size reduction which results in the formation of large number of grain boundaries, can be utilized for sensing application (Mitra *et al*., 1998; Sivalingam *et al*., 2011b; Jesen *et al*., 2008; Wang *et al*., 2011). However, limited literature data exists on the use of materials prepared by mechanical size reduction for sensing applications. In the present work, fine particles of SiO_2 and TiO_2 were prepared by stirred bead milling and have been tested for their ability to sense oxygen.

MATERIALS AND METHODS

Titanium dioxide (TiO_2) powder was procured from Qualigen Fine Chemicals, India. Well-screened, ground and sieved river-bed sand was used for preparation of silica particles (SiO_2). The pellet and thin film form of TiO_2 and SiO_2 materials were synthesized using stirred bead milling and spray pyrolysis technique.

Synthesis of pellet: The equipment and the procedure for stirred bead milling are available in our earlier publication (Manikandan *et al*., 2012a, b), with the exception being the termination of grinding after 6 h of coarse grinding. The suspensions were dried to produce particles of silica and TiO_2 for preparation of film and pellet. Apart from this, silica particles were made into pellet using the tablet punching machine (Khera Instruments, Delhi). The mass of a single pellet was found to be 0.325 g.

Synthesis of thin films: The obtained SiO_2 and TiO_2 particles from the bead milling process were dispersed in water, to form a solution. The dispersed SiO_2 and TiO_2 particles was sprayed using an indigenous spray chamber, discussed by Sivalingam (Sivalingam *et al*., 2012a). Sensing studies were carried out in a custom-made test rig as reported earlier.

RESULTS AND DISCUSSION

Microstructural studies: Figure 1 shows the Scanning Electron Microscope (SEM) micrograph of SiO_2 particles produced by stirred bead milling. Figure 2 shows the SEM micrographs of TiO_2 particles produced by stirred bead milling. Both the Fig. 1 and 2 show that the particles are agglomerated and irregular in shape. This can be attributed to the possible particle-particle interaction due to the high particle concentration in suspension during bead milling. The particle shape is irregular but the surface

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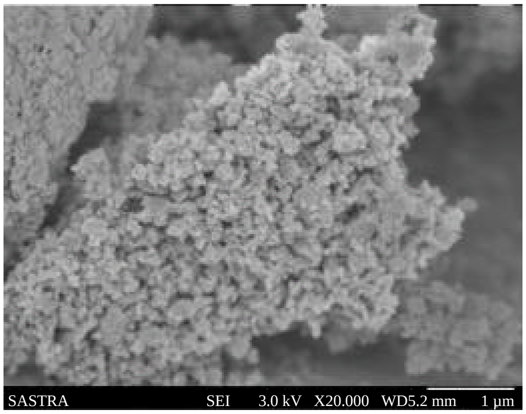

Fig. 1: SEM image of SiO_2 particles obtained from stirred bead milling

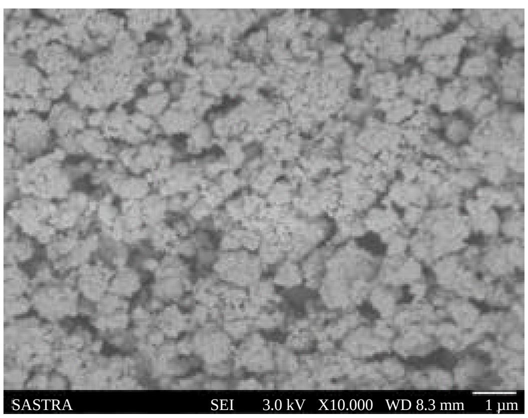

Fig. 2: SEM image of TiO_2 particles obtained from stirred bead milling

contains several fractures and grain boundaries which are expected to increase the surface area (Lu *et al*., 2008; Zheng *et al*., 2000; Slunecko *et al*., 1992).

An attempt was made to prepare SiO_2 film by spray coating using the silica dispersion. Usually this technique increases the semiconductor behavior of substance by the oxidation process with atmosphere. Substrate temperature, chemical kinetics of precursor solution and annealing are important for the formation of metal oxide sample, particularly n-type or p-type. Figure 3 shows the SEM image of as deposited SiO_2 thin film which shows that uniform formation of nanoparticle on the substrate with pores. The films were annealed for various time periods to observe changes in the microstructure of the film. Figure 4 shows the SEM

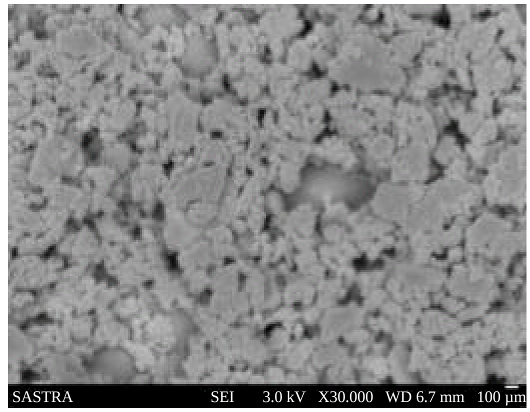

Fig. 3: SEM image of As deposited SiO_2 thin film

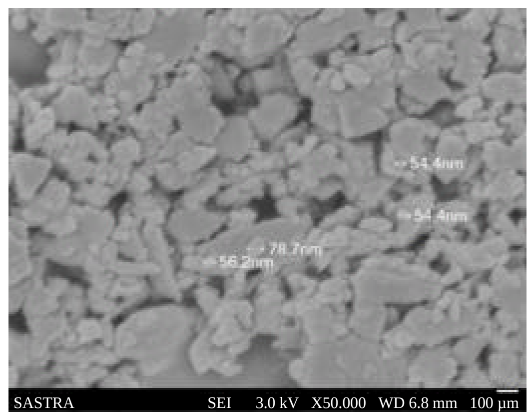

Fig. 4: SEM image of 1 h annealed SiO_2 thin film

micrograph of 1 h annealed SiO_2 thin film and Fig. 5 shows the SEM micrograph of two-hour annealed SiO_2 thin film.

It may be observed from Fig. 3-5 that there are no substantial changes in the morphology of films as a result of annealing. The annealed image of Fig. 5 showed that grain sizes are average of 50 nm. Thermal treatment of SiO_2 thin film had more crystallinity, when compared to as deposited and one hour annealed film samples and pore size have reduced. The pellet (Fig. 1) and thin film (Fig. 3-5) image of SiO_2 particle shows significant changes with respect to structural morphology.

Response towards oxygen sensing: Oxygen is an oxidizing gas which means a strong electron acceptor. Figure 6 shows the response of silica pellet towards 1000 ppm of oxygen. The response of silica pellet towards 1000 ppm of oxygen shows decrease in resistance upon exposure to

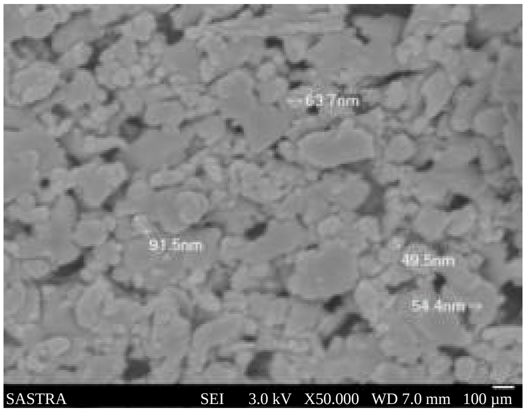

Fig. 5: SEM image of 2 h annealed SiO_2 thin film

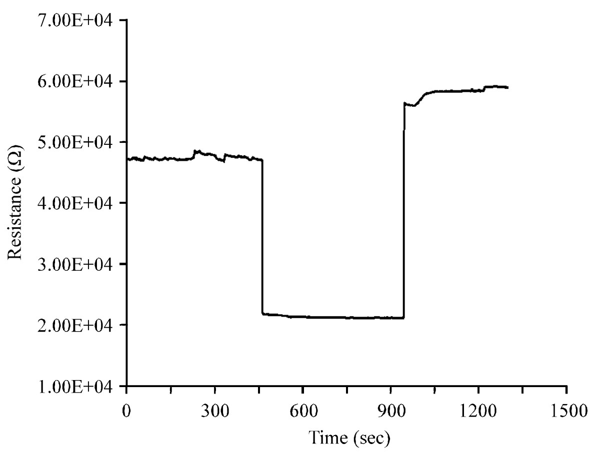

Fig. 6: Response of silica pellet upon exposure to 1000 ppm of oxygen

oxygen. If the resistance of material decreases with the interaction of oxidizing gas, it corresponds to a p-type material. Interaction of oxygen with n-type material decreases the conductance of the material due to the pulling of electrons from the surface (Sivalingam *et al*., 2012b). However, the decrease in resistance in the case of SiO_2 pellet, is a clear indication that it is p-type material. The process of oxygen adsorption reduces the number of electrons and increase the hole concentration in the conduction band. The ratio of change in carrier concentration decides the sensing response of a material. The response of the material towards oxygen can be defined as the ratio of resistance measured in atmosphere and oxygen i.e., $R = R_{(atmosphere)}/R_{(oxygen)}$ (Kannan *et al*., 2010) with the measurements being made in a closed chamber (Sivalingam *et al*., 2012b). The response of SiO_2 pellet was found to be approximately 2.18.

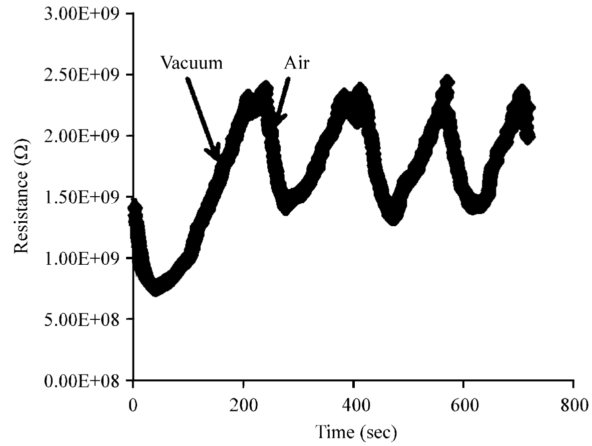

Fig. 7: Response of TiO_2 pellet to air at 100°C

Similar to silica pellets, TiO_2 pellets were also considered for oxygen sensing; however, it did not respond to oxygen at room temperature. However, the same pellets showed a good response towards oxygen when temperature was increased to 100°C. The response of TiO_2 pellet to air at 100°C is shown in Fig. 7. The response shows a reduction in resistance with exposure to oxygen, clearly showing a p-type behavior. Increase in resistance during the oxygen ambience, is the behavior of a n-type material. At low temperature, TiO_2 surface do not have the ability to adsorb oxygen, because of minimum number of electrons in the conduction band. At high temperature, thermal energy excites electrons from the valence to conduction band which act as active sites for oxygen in the atmosphere. Compared to silica, TiO_2 showed poor sensing performance with a response of approximately 1.9. In TiO_2, we need to initiate the oxygen sensing process by applying the thermal energy but SiO_2 senses oxygen at room temperature. TiO_2 is an n-type material (Ramamoorthy *et al*., 2003; Li and Chen, 1996). The decrease of resistance with oxygen exposure as shown in Fig. 7 implies that, TiO_2 pellet behaves as p-type material, indicating that preparation method alter the material property. The experiments were repeated several time to confirm the reduction in resistance with oxygen exposure. The experiments will be carrying with several other gases to confirm the electrical properties. Although, p-type nature can be inferred from the reduction in resistance, other methods such as Seebeck coefficient, sheet resistance (Rahmani *et al*., 2009), Hall measurement (Chen *et al*., 2005; Maqsood *et al*., 2012) and four probe (Rahul *et al*., 2011) are required for positively ascertaining the electrical properties of the samples. In contrast to silica and TiO_2 pellets, silica and TiO_2 thin films prepared using spray pyrolysis technique did not show any response towards oxygen.

CONCLUSIONS

Silica and TiO_2 pellets were produced by stirred bead milling method from the fine particles of sand and commercial TiO_2 powders and the thin films were prepared using spray pyrolysis technique. Both the silica and TiO_2 pellets showed response to oxygen, while, the thin films did not show any response to oxygen. Comparatively, TiO_2 pellet has poorer response than silica pellet and does not work at room temperature. The reduction in resistance with exposure to oxygen showed that both are p-type materials. With further experimentation, the material and pellet preparation may be fine-tuned to fabricate oxygen sensors based on these materials.

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