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Methane sensing studies of ex-situ oxidized sputtered V_2O_5 nanostructured films: Effect of post oxidation duration

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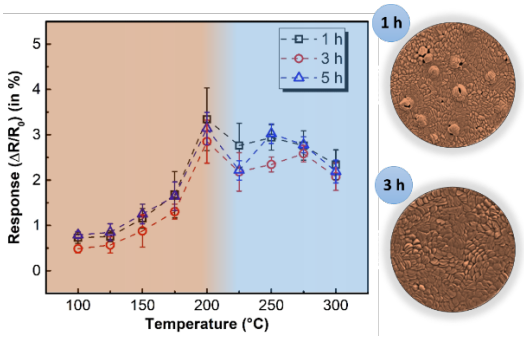
Article

ABSTRACT

The effect of microstructural modifications of V_2O_5 thin films, obtained through alterations in post oxidation duration, on methane sensing behavior is reported for the first time. Three different oxidation times viz., 1 h, 3 h and 5 h yielded varied microstructure and vibrational properties as evident from XRD and Raman investigation. These changes in properties manifest as differences in gas sensing behavior. Methane sensing properties of V_2O_5 was investigated in temperature range from 100 to 300 °C and optimum operating temperature of 200 °C was identified for all three samples. Films oxidized for 1 h showed the highest response due to favorable surface conditions which are discussed. These results will help in tailoring microstructure towards device level application processes.



Keywords: Vanadium Pentoxide, RF sputtering, microstructure tailoring, oxidation time, methane sensing

INTRODUCTION

The gas sensing properties of a material are affected by many parameters starting from its synthesis, post-deposition treatments and also operating conditions while sensing. These parameters provide us the option to alter the sensing behavior to suit our desired applications. Much of the device level applications require stringent quality checks at every level. One of the primary objectives during synthesis stage is reproducibility and large-scale synthesis capability so that wastage is minimized. The use of sputtering in such fabrication industries is well known. The added ex-situ heat treatment stage gives us the flexibility in tailoring the thin film characteristics with a fixed infrastructure setup.

Among the several transition metal oxides, oxides of vanadium have attracted more attention due to multiple valency ranging from +2 to +5. Vanadium oxide can exist in several stoichiometric forms as well as sub-stoichiometric states. Vanadium pentoxide (V_2O_5), among them is the most stable state, in particular is an interesting oxide of vanadium. There is tremendous scope for research due to its layered 2D structure that offers several permutations of oxygen vacancies and defects. A metal insulator transition around 257 °C is also reported which leads to several applications thereby showing potential to be integrated to the microelectronics industry.[1] It has been synthesized by variety of methods ranging from physical vapor deposition, chemical vapor deposition, pulsed laser techniques, sol-gel, chemical precipitation etc. Sputtering has been used in this present study due to the reasons mentioned earlier.

V_2O_5 has been investigated as gas sensing material both in pristine form[2-4] as well as in mixtures with other metal oxides.[5-7] There are numerous reports of nanostructured V_2O_5 used for detection of ammonia,[8] ethanol[9] and nitrogen oxides[10] among other gases. There has been only limited interest towards methane sensing by pristine V_2O_5.[11,12] The present study aims at establishing a correlation between microstructure altered through post deposition oxidation time and methane sensing behavior of sputtered V_2O_5 nanostructured films. This would help to tailor the microstructure towards better sensing response. This is the first report of such study to the best of our knowledge.

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EXPERIMENTS

Metallic vanadium films were deposited by magnetron sputtering technique on to Si (100) wafers containing SiO_2 films grown by thermal oxidation. These substrates were selected due to their high temperature stability to withstand the post oxidation process and electrically non-conducting property that is crucial for sensing studies. The substrates were cleaned using organic solvents followed by rinsing with de-ionized water in an ultrasonic bath and dried using dry nitrogen gas. The base pressure of the sputtering chamber was 3×10^{-6} mbar and the working pressure was maintained at 4.2×10^{-3} mbar by flowing argon gas. A pressured control system with a throttle valve was used to maintain the working pressure. The source material was a metallic vanadium target with 99.99% purity from Testbourne, UK.

Magnetron discharge was sustained at an rf power of 50 W for a deposition time of 12 min. Film deposition at this condition yielded a desired film thickness of ~100 nm. These metallic films were subjected to post oxidation treatment at 500 °C for three different heating durations of 1 h, 3 h and 5 h. After annealing the film thickness was in the range of 150±20 nm. X-ray diffraction was carried out to identify the phase and crystallinity of the samples in grazing incidence geometry using an Equinox 2000 diffractometer from Inel. A Zeiss scanning electron microscope (FE-SEM, SUPRA 55) was employed to observe the surface morphology. A Renishaw laser Raman spectrometer was used to study the vibrational modes with Ar^+ laser source (514.5 nm) and a thermoelectric charge coupled device (CCD) detector.

Gas sensing experiments were performed in a custom-built set up with a stainless-steel chamber where a heater stage with a PID controller is installed. The sensing tests were done in dynamic condition with the sensing chamber being fed with the gas mixture through mass flow controllers and pumped using a dry scroll pump.

A gas mixture consisting of UHP (99.999%) Nitrogen and 10 % UHP Oxygen (99.999%) as the carrier gas in the background was used. Methane gas mixing ratio was varied to achieve

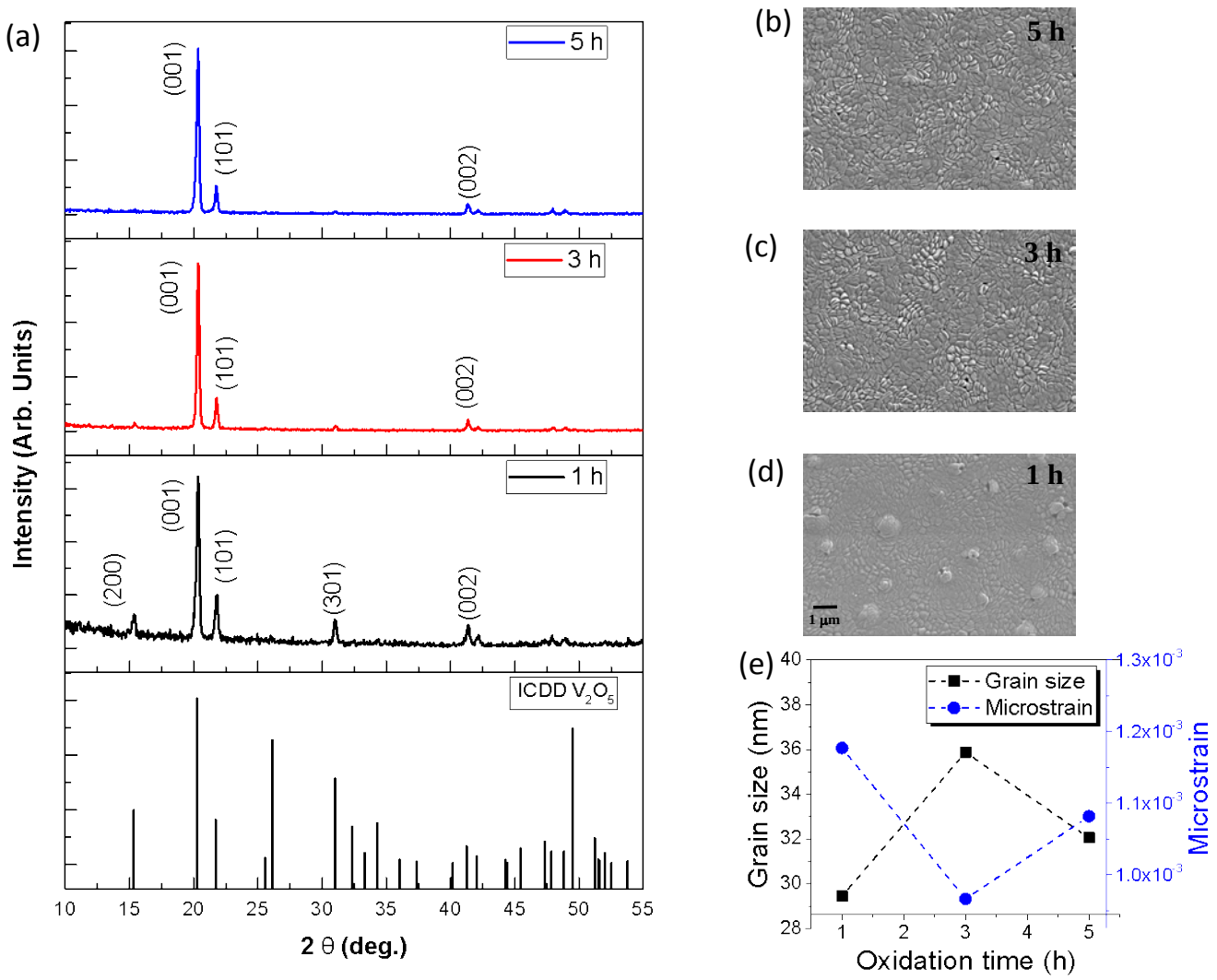

Figure 1. a) GIXRD patterns of vanadium oxide films oxidized for 1 h, 3 h and 5 h at 500 °C. ICDD pattern corresponding to card number 00-041-1426 is shown for comparison. SEM images of the samples at **b)** 5 h **c)** 3 h **d)** 1 h **e)** Variation of grain size and microstrain versus oxidation time.

different concentrations while the sensing chamber was maintained at a constant pressure of 15 mbar. At each temperature (at which the sensing experiment was done), the sample resistance was allowed to stabilize before exposing to the target gas. Change in resistance was recorded using an Agilent B2911A source measure unit. Measurements were done at methane concentrations of 100 to 500 ppm and the operating temperatures are varied from 50 to 250 °C.

RESULTS AND DISCUSSION

Grazing incidence X-ray diffraction pattern of the films are shown in figure 1. The diffractograms show that films formed are well crystallized and the diffraction peaks are found to match with the reference pattern ICDD: 00-041-1426 confirming the presence of orthorhombic V_2O_5 phase (S.G.: *Pmmn*). All the samples show a strong diffraction peak at 2θ of 26° corresponding to (001) plane. Other smaller peaks corresponds to (101), (200), (301) and (002) diminishes upon increasing the duration of the post oxidation treatment. Compared to the reference pattern from ICDD, the sputter deposited and post oxidized films have preferred orientation along (001) plane. This indicates the growth of V_2O_5 films preferentially along *c*-axis perpendicular to the substrate plane. Grain size was estimated from Debye-Scherrer formula and found to increase from 29 nm to 35 nm upon increasing the post oxidation time from 1 h to 3 h. Upon further increase in the post oxidation time to 5 h, the average grain size decreases to 32 nm. Micro strain was calculated from the XRD peak position and the peak width and the same is plotted along with grain size in figure 1 (e). Post deposition heat treatment can result in a range of consequences in microstructure including grain growth, modification in surface morphology, and relaxation of micro strain, reduction in voids and pores and densification. In some cases, it may result in structural reorganization such as favorable formation of certain phase or orientation of grains along certain crystal planes. Increase in the grain size upon heat treatment could be related to the defect annihilation process and lattice relaxation by reducing the micro strain.

Morphological analyses using SEM shows chrysanthemum like nanostructures for all the samples. Figure 1 (b), (c) and (d) display the respective SEM image for the sample undergone post oxidation treatment for 5 h, 3 h and 1 h, respectively. Upon closer look, voids can be seen between the flower structures. The void fraction decreases while increasing the post oxidation duration. The petal like structures get larger and denser for longer oxidation times. This observation is consistent with the increase in grain size concluded from XRD analyses.

To evaluate the bonding nature and formation of V_2O_5, Raman spectroscopy analysis was carried out and the spectra are shown in figure 2. The unit cell of V_2O_5 is made of VO_5 square pyramids sharing their edges and corners. Group theoretical analysis of orthorhombic polymorph, α-V_2O_5 shows that there are 21 zone center (at Γ point) Raman active modes. In the present study, the experimentally observed Raman modes are at the frequencies of 103, 144, 198, 284, 304, 404, 481, 701, and 994 cm^{-1}. The break in the Raman spectrum corresponds to substrate peak (silicon at 521 cm^{-1}). The structure of V_2O_5 consists of three structurally inequivalent O atoms namely, vanadyl (O1), bridge (O2) and chain (O3) oxygen with coordination numbers one, two and three respectively.

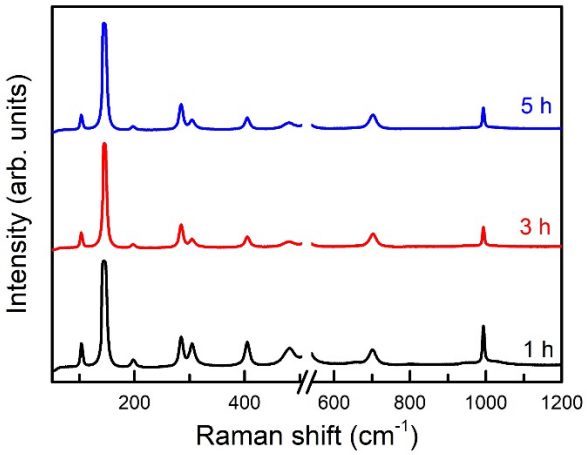

Figure 2. Comparison of Raman spectra of films post oxidized for 1 h, 3 h and 5 h duration.

The three low frequency modes at 103, 144 and 198 cm^{-1} are chain translation modes along *c, b and a* – axes respectively. The mode at 284 cm^{-1} is due to the deflection of V–O2–V and V–O1 along *b*–axis. The modes at 304, and 701 cm^{-1} appear as a result of V–O3–V stretching vibrations along *c* and *b*– axes respectively. The peak at 404 cm^{-1} arises due to the deflection of V–O1 along *a*–axis. The mode at a frequency of 481 cm^{-1} is reported to be due to the deflection of V–O2–V along *c*– axis. The highest frequency mode at 994 cm^{-1} is an exclusively out of plane vibrational mode due to the stretching vibration of V–O1 along *c*– axis.[13,14] Upon annealing, O vacancy defects in the films are expected to be annihilated and the degree of defect annihilation would increase with annealing duration.

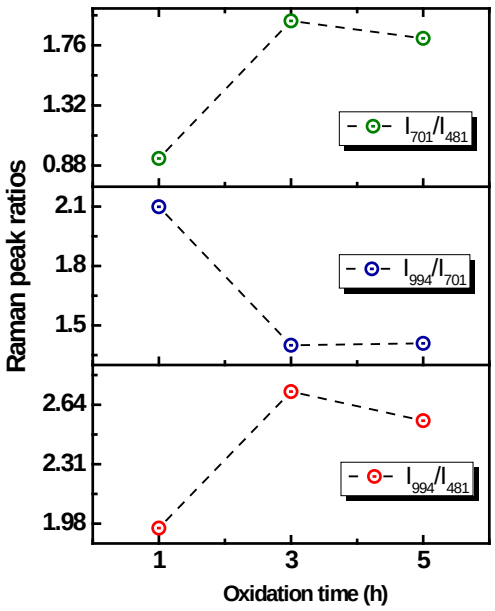

Figure 3. Variation of Raman peak ratios as a function of post oxidation time.

As discussed before the vibrational modes at 994, 701 and 481 cm^{-1} are correlated to the vibration of V–O1, V–O3 and V–O2 respectively. Figure 3 shows the ratio of selected Raman peak intensities for the three samples. Increase in the intensity ratios I_{701}/I_{481} and I_{994}/I_{481} indicates that there are more O1 and O3 vacancies in the sample oxidized for 1 h than the other samples.

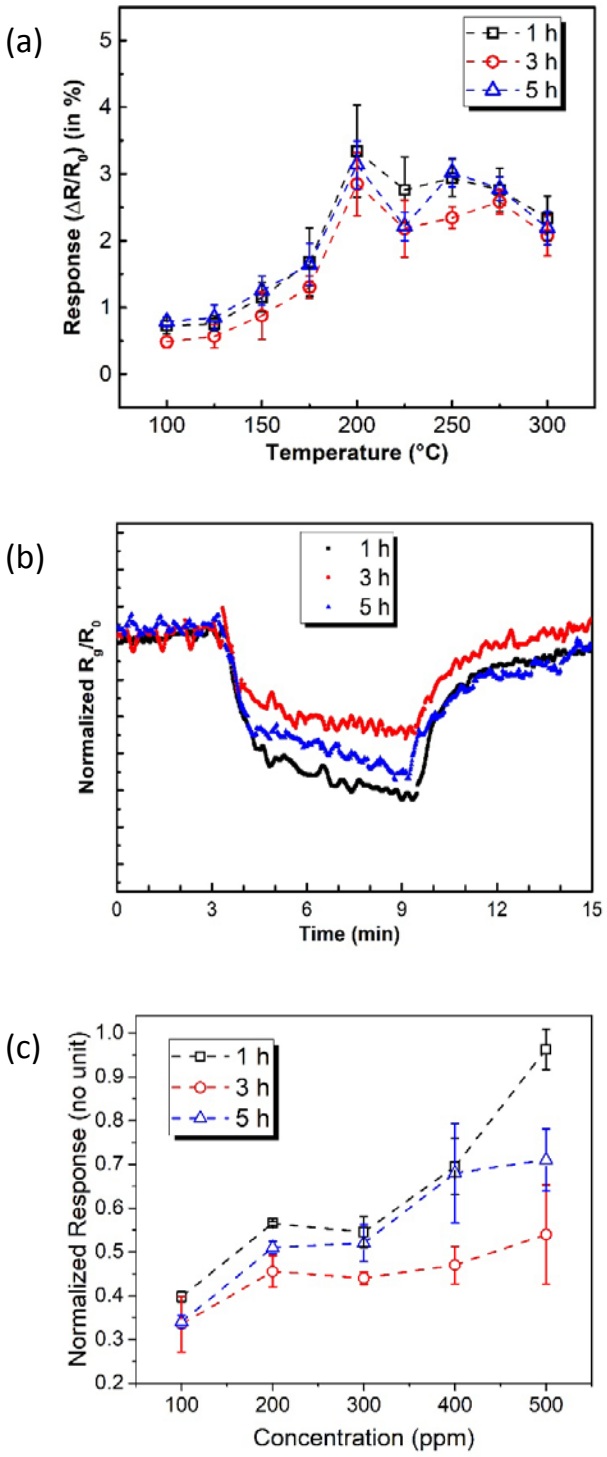

Figure 4. a) Temperature versus response curve comparison **b)** Normalized response transients for 3 films **c)** Response versus concentration.

At the same time, there is a decrease in the ratio I_{994}/I_{701} that is observed with the oxidation time, which indicates that the O3 vacancy defects are prominent in the sample annealed for 1 h. It is observed from the XRD pattern that the strain in the samples are in the order 1 h> 5 h> 3 h as shown in figure 1(e), which is reflected in the Raman spectrum also, because the strain in the samples could be due to the presence of the defects.

Sensing response of *ex-situ* oxidized V_2O_5 thin films for CH_4 gas at different concentrations from 100 to 500 ppm were studied.[18] The sensor response was studied in the temperature range 100 to 300 °C in steps of 25 °C (figure 4a). The experiments were repeated for at least five times and the stability of the sensing behavior was observed and was found to be reproducible over several months. A typical sensing transient displaying the change in resistance for gas exposure is shown in figure 4b. It is observed that the drop in resistance is highest for samples oxidized for 1 h.

Samples oxidized for 3 h showed the lowest change and that for 5 h showed a change in between. The typical response and recovery times of the sensor was around 1 min and 1.5 min respectively. Upon increasing the temperature, the sensing response for all the samples (defined as the ratio of change in resistance to the original resistance) increases and reaches a maximum at around 200 °C and begins to drop down till 300 °C. The samples showed a maximum sensing response of 3% for 500 ppm at 200 °C. There is a local maximum around 250 °C. This could be correlated to the fact that V_2O_5 is known to have a reversible surface phase transition from semiconductor to metallic phase around 257 °C. Similar observations have been reported earlier[11,12] wherein the increase is attributed to change in surface electrons contributing to increased sensor response.

While comparing sensing performance between the samples, the one post oxidized for 1 h shows higher response than others at all temperatures and concentrations (figure 4c). This trend can be directly related to the variation in microstructure observed from XRD and Raman spectroscopy analyses. Grain size plays a very critical role in sensing mechanism. It is a well-established fact that smaller grain size is better for sensing.[15] In *n*-type semiconductors, electrons are the major charge carriers and electron depletion layer in the surface plays a pivotal role in sensing mechanism. Adsorption of the analyte molecules alters the potential barrier at the grain boundaries. Thus, materials with smaller grain size i.e., more grain boundaries show larger variation in resistance to gas exposure. Moreover, as seen it the SEM images (figure 1a-d), the samples subjected to 1 h of *ex-situ* heat treatment show more pores in the surface morphology. When the porosity is higher, the surface area available for the chemical reaction would also increase as the analyte gas can diffuse through the pores and get absorbed[16]. A study on the role of chemical accessibility in sensing is reported by Yamazoe et al.[17] This explains the higher sensor response of sample subjected to 1 h of heat treatment.

From the observations from Raman spectrum, there are more dangling bonds on the surface of V_2O_5 thin film annealed for 1 h than the thin films oxidized for 3 h and 5 h, as result of the oxygen vacancies, particularly O3 vacancy. Since the chain oxygen, O3

is bonded to three V atoms in the stable structure, the vacancy of O3 offers more active sites for the adsorption of analyte gas molecules. As a result, the thin films that are post oxidized for 1 h showed more sensor response than the other samples and the trend of the change in sensor response is in line with the observations from the analysis of Raman spectrum and XRD pattern. The observation from above results support the favoured application of sputter deposited *ex-situ* oxidized nanostructured V_2O_5 as promising sensor for detection of methane gas.[19,20]

Conclusion

Methane sensing characteristics of sputter deposited *ex-situ* oxidized nanostructured V_2O_5 films are reported. A sensor response of 3% for methane concentration of 500 ppm was obtained at a temperature of 200 °C and it drops slightly for higher temperatures. From XRD and Raman spectroscopy analyses, it was found that the microstructure of the thin films markedly varies upon varying the duration of post deposition heat treatment. The comparative sensing response shows a direct correlation with the microstructure. Sample subjected to shorter heat treatment time was found to have O3 oxygen vacancy sites where oxygen atom triply co-ordinates with vanadium. It can be concluded that O3 oxygen vacancies play a determining role in methane sensing.

Conflict of Interest

Authors declare no conflict of interest.

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