

Nanocrystalline $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ Xerogel Thin Film for Gas Sensing

M. S. Al-Assiri, M. M. El-Desoky, Ahmed A. Ibrahim, M. Abaker, A. A. Bahgat

Abstract—Nanocrystalline thin film of $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ xerogel obtained by sol gel synthesis was used as gas sensor. Gas sensing properties of different gases such as hydrogen, petroleum and humidity were investigated. Applying XRD and TEM the size of the nanocrystals is found to be 7.5 nm. SEM shows a highly porous structure with submicron meter-sized voids present throughout the sample. FTIR measurement shows different chemical groups identifying the obtained series of gels. The sample was n-type semiconductor according to the thermoelectric power and electrical conductivity. It can be seen that the sensor response curves from 130°C to 150°C show a rapid increase in sensitivity for all types of gas injection, low response values for heating period and the rapid high response values for cooling period. This result may suggest that this material is able to act as gas sensor during the heating and cooling process.

Keywords—Sol gel, Thermoelectric power, XRD, TEM, Gas sensing.

I. INTRODUCTION

SEMICONDUCTING oxides films like V_2O_5 , ZnO, WO_3 , MoO_3 etc. have been used in gas sensors for sensing many pollutants in air at trace levels [1], [2]. Control of microstructure is one of the important factors in improving the sensor features, as sensor action is a surface phenomenon. Nanostructured materials offer high specific surface area and being perfect for this service. Efforts are made to fabricate nanocrystalline oxides by many soft chemical methods. These nanocrystalline films would subsequently be used in the fabrication of thick films, which are the generally used configuration in chemical sensors [3].

Nanocrystalline vanadium pentoxide is normally a non-stoichiometric material, which is known for its catalytic properties in oxidation reactions. As it is an electric conductor when oxygen vacancies are present, the purpose of this study is to determine the effect that reducing gases have on the conductance of vanadium pentoxide films [4], [5]. Reducing gases such as hydrogen increases the conductance of vanadium pentoxide films. This change can be reversed when the film recovers in a reducing-gas free oxygen-rich atmosphere. In conjunction with the weight measurement, it can be concluded that oxygen is lost by the vanadium

pentoxide films and again resorbed in the recovery phase [6], [7].

On the other hand, layered intercalation nanomaterials such as vanadium pentoxide (V_2O_5) nanocrystalline films have been receiving significant attention owing to their applications in various fields such as energy-storage systems and sensors [6], [7]. Also, layered V_2O_5 are suitable as host materials such as alkali materials for intercalation chemistry because of their interlayer spaces in conjunction with their semiconducting properties enable them to act as cathodic materials for advanced lithium batteries, gas sensor etc. [8], [9]. Layered V_2O_5 can be partially reduced allowing an electron hopping process between vanadium ions in different valence states, namely V^{4+} and V^{5+} . The charge transfer is usually termed a 'small polaron hopping' (SPH) [10], [11]. Electrical properties of alkali- intercalated V_2O_5 nanocrystalline films were studied and reported in a number of publications and the results were due to the existence of two different valence states of vanadium ions namely V^{4+} and V^{5+} [12]-[16]. The electrical conductivity of these nanocrystalline films shows that all samples were semiconductor and increased with increasing alkali content [12]-[16].

In this paper, $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ xerogel nanocrystalline thin film was prepared by sol-gel technique. The nanostructural, and gas sensing properties for different gases such as hydrogen, petroleum and humidity were investigated.

II. EXPERIMENTAL

Xerogel nanocrystalline thin film of $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was prepared by sol-gel technique. This composition was synthesized from highly pure vanadium pentoxide (V_2O_5) (99.999%), and sodium carbonate (Na_2CO_3) (99.999%) aqueous solution. A film with different thicknesses of the investigated compound was prepared by the sol-gel technique (colloidal route). A batch of 2 g of V_2O_5 was dissolved in hydrogen peroxide (H_2O_2) at room temperature. The formed solution was stirred continuously using magnetic stirrer. The solution was then heated at 60°C, with uninterrupted continuous stirring while pH was kept at 2. The gel can be synthesized via the condensation of aqueous solutions of $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$. The obtained sols were deposited on glass substrates before complete gelation by the dip coating method, which was then left to dry in a clean air environment. The obtained films were tightly bonded to the glass substrate, this was obviously recognized if a mechanically scratch was intended. Measurements were conducted on the as-casted thin films without any intended heat treatments.

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X-ray diffraction patterns were obtained in order to identify the structure and the crystallite size of the prepared films using XRD-6000 Shimadzu (with Cu-K α radiation). The diffraction data were recorded for 2θ between 4° and 60° with a resolution of 0.02° . The surface morphology of the films was observed using a transmission electron microscope, TEM, (Jeol, Jem-1010) to investigate the crystal structure of particles in which a TEM observation was performed at an accelerating voltage of 70 kV. Surface morphology, chemical and phase composition of the materials were tested by Scanning Electron Microscopy (JEOLI-5800LV) equipped with an x-ray micro-analyzer (EDS-S60 DX90). Thermoelectric power (S) above room temperature was measured where the type of conduction was found to be an n-type semiconductor. Infrared (IR) spectra of the glass samples were measured from 400 to 2000 cm^{-1} by a conventional KBr pellet method on a Fourier transform infrared (FT-IR) spectrometer (Perkin-Elmer 1760 X). The dc electrical conductivity was measured by the two probe method using silver past electrodes in coplanar geometry parallel to the substrate surface. The sample is placed inside a special Pyrex chamber which can be evacuated as well as filled with different gases. Ambient air was used both as a reference gas and as a diluting gas to resemble actual ambient condition. A schematic diagram of the measuring cell is shown in Fig. 1. Measurements were conducted under a pressure of one atmosphere unless vacuum is required.

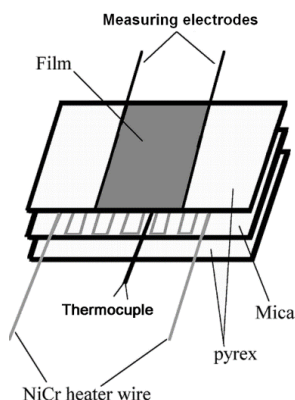


Fig. 1 Schematic illustration of the electrical conductivity measurement cell

III. RESULT AND DISCUSSION

A. XRD

XRD pattern of the present nanocrystalline thin film of $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ is shown in Fig. 2. From this figure the XRD peaks which are observed and identified are (001), (003), (004), and (005) indicate a preferred orientation. These results are in good agreement with the JCPDS card: 40-1296, where the lattice constant for pure $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was evaluated using Rietveld refinement program [17]. The XRD patterns of the films show the (001) peak at about $2\theta = 7.2^\circ$, $d = 1.24$ nm indicating a high preferential c-axis orientation and is a characteristic of the one dimensional stacking of the vanadium pentoxide xerogel ribbons parallel to the glass substrate

surface while vanadium oxygen layers are formed by tangled fibers and connected by water molecules [17]. The average crystallite sizes, D , of the precipitated nanocrystals were calculated according to Sherrer's formula [18];

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

D was found to be in the range of 7.5 nm. Where $k \sim 1$, λ (nm) represents the wavelength of Cu-K α radiation; θ is the Bragg angle of the X-ray diffraction peak and β represents the corrected full width at half maximum of the diffraction peak in radians. These results indicated a c- axis orientated nanocrystalline film of $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, i.e. normal to the substrate surface, and which can be prepared without any difficulties by the sol-gel technique.

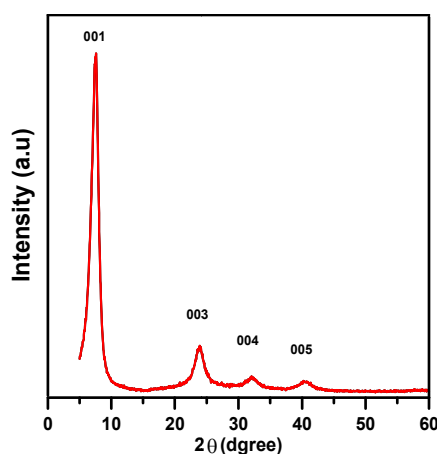


Fig. 2 Room-temperature XRD for $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ nanocrystalline film

B. TEM and SEM

Fig. 3 shows the TEM image of $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ nanocrystalline film. It is found that the film surface was relatively smooth with an average nanocrystalline size of 8 nm in close agreement with XRD results. It shows also that this film has a thin uniform layer stacking, indicating that $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ nanocrystalline clusters are not so much far from each other and are interacting with each other through an even weak force [17]-[19]. This interesting shape within the nanoscale dimension leads to the exposure of a large fraction of the atoms to the surface, making these materials promising candidates for the development of new functionalized materials.

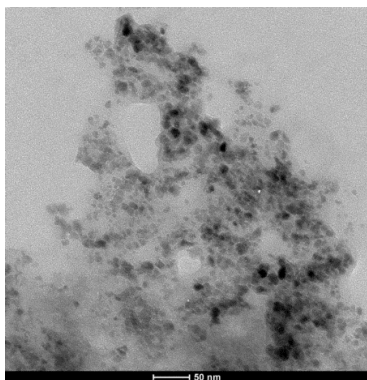
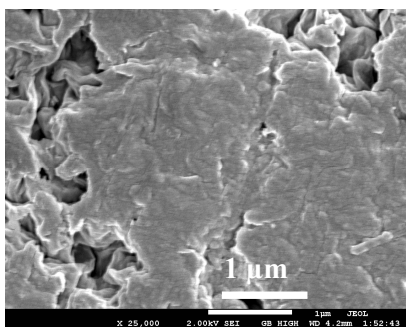
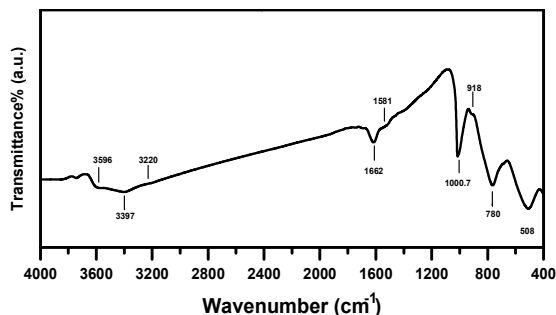
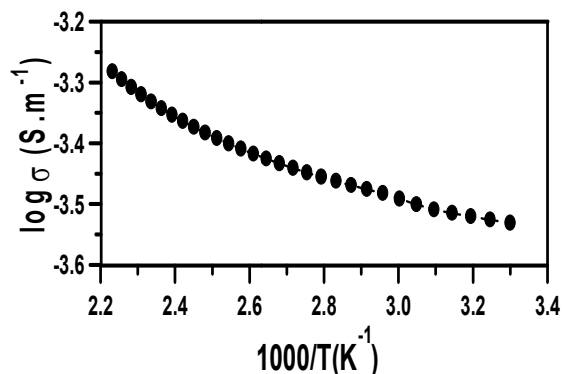
Fig. 3 TEM for $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film

Fig. 4 shows the SEM image of the present $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film. From the figure it is clear that a highly porous structure is created, with submicron meter-sized voids presented throughout the sample. The pores in the film are all in a “spherical”-type shape and are highly separated. Such a structural architecture closely resembles mesoplates stacked in a roach fish skin like, epidermis. In this mechanism, self-organization into layers on the surface of which the concentration of inorganic species takes place.

Fig. 4 SEM image for $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film

C. FTIR Spectrum

The FTIR spectrum of the film prepared under normal conditions by sol gel technique is shown in Fig. 5. Room temperature FTIR spectrum shows several absorption bands for the $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film. The IR spectrum of this composition is found to be similar to that of $\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film [21]. In order to identify different structural groups, the absorption bands in the FTIR spectrum are marked as shown in Fig.5 according to refs.[20], [21]. The band at 508 cm^{-1} is characteristic of the stretching vibration of the $\text{V}-\text{O}_2$ bond, while the bands at 780 cm^{-1} and 918 cm^{-1} may be assigned to VO_4 tetrahedra and VO_5 pyramid bond stretching. The band at 1007 cm^{-1} may be attributed to the stretching mode related to the shortest vanadium–oxygen bond $\text{V}=\text{O}$ [13]. On the other hand, different water species are marked, where the absorption bands of the vibration modes 1400 and 1650 cm^{-1} and absorption bands of the stretching vibration modes between 3100 and 3650 cm^{-1} of OH , H_2O , H_3O species are indexed as shown in Fig. 5 [21].

Fig. 5 IR spectra for $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline filmFig. 6 Temperature dependence of dc conductivity (σ) for $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film

IV. SENSING PROPERTIES

Fig. 6 shows a semiconducting temperature dependence of the electrical conductivity $\sigma(T)$, for $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film, which is the best being described by Mott formula [10,11].

$$\sigma = \sigma_0 \exp(-W/kT) \quad (2)$$

where σ_0 is a pre-exponential factor and W is the activation energy. The activation energy (W) was obtained from the least square straight line fit of the data at high temperature. It shows a linear temperature dependence up to a critical temperature $\theta D/2$ (θD Debye temperature) and then the slope changes with deviation from linearity and the activation energy (W) is a temperature dependent. Such a behavior is a feature of SPH [10], [11]. This semiconducting property of $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film results from the existence of two different valance states of vanadium ions namely V^{4+} and V^{5+} where the electronic conductivity takes place by electron hopping from low to higher valance state. The conductivity thermal activation energy found here, 0.10 eV , is in close resemblance to the value of 0.18 eV found in Ref. [13].

Thermoelectric power (S) of $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film has been investigated as a function of temperature. Fig. 7 shows the temperature dependence of thermoelectric power of the present nanocrystalline film. The general expression for S in the case of nanocrystalline semiconductors, where carriers are excited to extended states

beyond the mobility edge, is assumed by [22]:

$$S = \pm \frac{k}{e} \left[\frac{\Delta E_s}{kT} + A \right] \quad (3)$$

where A is a small constant which represents the thermal energy transported by carriers, e is the electronic charge k Boltzmann's constant and ΔE_s is the activation energy associated with conduction. On the other hand, the sign of the thermoelectric power was found to be negative indicating that the conduction takes place by electrons to the conduction band. Hence the sample under test is n-type semiconductor. This is consistent again with SPH mechanism [10], [11]. No evidence of ionic contributions was observed, such as in many intercalated alkali vanadium xerogels [12], [13], [17].

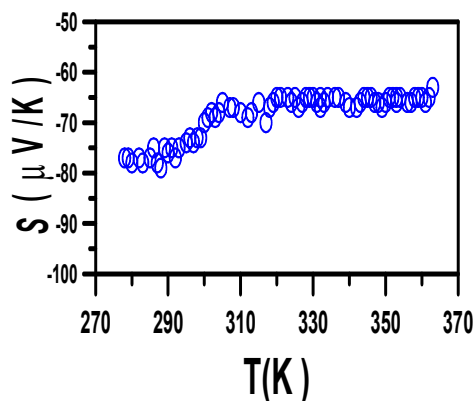


Fig. 7 Thermoelectric power(S) as a function of temperature for $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film

The sensing properties of the metal oxides are based on reactions between metal oxides and gases in the atmosphere. These reactions create changes in the electrical properties of semiconductor. Several parameters such as crystallite size, film thickness, porosity, amount and nature of dopants, catalysts and surface states are known to be significant in improving the gas sensitivity of the sensors [5], [23]. The gas sensing properties were estimated by measuring the changes of resistance of the sensors, before and after the sensed gases were introduced [23]. The measurements were taken at operating temperatures ranging from 30°C to 180°C. Figs. 8 (a) and (b) show the relationship of the sensitivity and operating temperature heating and cooling for $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film at different gases. Here, the sensitivity was defined as R_g/R_a , where R_g and R_a are the resistances of the film in hydrogen, petroleum and humidity gases and in ambient air, respectively [23]. It is interesting to see that the response values of the $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film sensor were larger than 0.5 at different gases, which means that the resistances of the sensor increase upon exposure to hydrogen, petroleum and humidity gases. It is well known that the semiconductor metal oxides are usually classified as n-type or p-type according to the direction of resistance change when they are exposed to a reducing gas

such as H_2 . For n-type semiconductor, the chemisorbed oxygen on the surface reacts with the reductive gas species and the electrons trapped by oxygen are released into the conduction band of the semiconductor, leading to a resistance decrease [24], [25]. With regard to p-type semiconductor, the opposite change in the resistance is observed upon exposure to a reducing gas due to the combination of holes with electrons released from the surface reaction. Here, the sample under test is n-type semiconductor as observed in thermoelectric power result. According to the above discussion, $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film sensor showed the typical n-type semiconducting behavior in the operating temperature range. It can be seen that the sensor response curve from 40-80°C and from 130 to 150°C shows a complex pattern; rapid increase in sensitivity for all gas injection, low response values for heating period and the rapid high response values for cooling period [25]. This variation between response values for heating and cooling period can be understood by the release of adsorbed atmospheric gasses as due to the heat treatment and/or measurements up to 180°C [5].

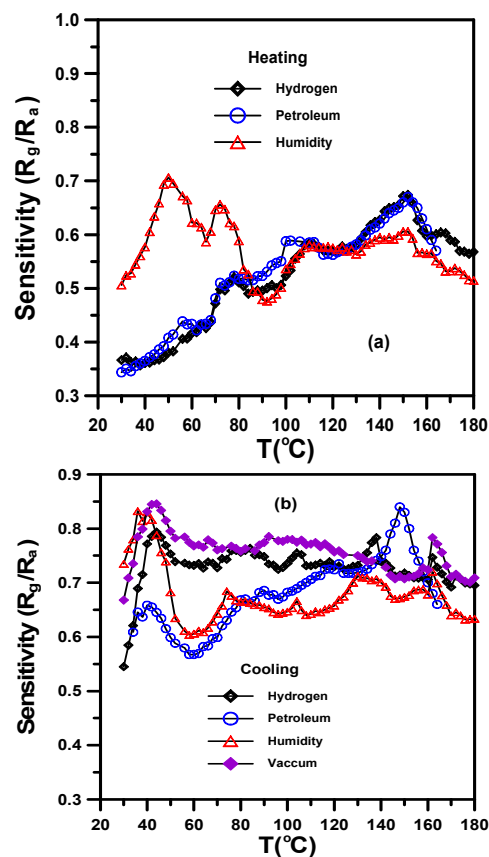


Fig. 8 Sensitivity as a function of temperature for (a) heating and (b) cooling of $\text{Na}_{0.1}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ nanocrystalline film at different gases

Generally, a reducing gas such as H_2 reacts with the negatively charged surface oxygen and decreases the resistance by the injection of an electron; therefore the current arises. It can see that the sensor response at operating

temperature of about 40-80°C and 130-150°C shows high response than at intermediate temperatures. On the other hand, at low operating temperatures for heating period, response of the film for different gases is restricted due to slow chemical reaction because the gas molecules do not possess sufficient thermal energy to react with the surface adsorbed oxygen species. In fact, during adsorption of atmospheric oxygen on the film surface, a potential barrier to charge transport is developed. At higher operating temperatures for heating and cooling period, the thermal energy obtained is high enough to overcome the potential barrier and thus electron concentration is increased significantly due to sensing reaction, which in turn leads to an increase in response of the film [24], [25]. At low temperature for different gasses the maximum sensitivity is 0.85 in the temperature range 40–80°C for heating and cooling period. At high temperature for different gases, the sensitivity is maximum i.e. 0.6-0.85 at 130-150°C operating temperature. The maximum response is attributed to the availability of sufficient adsorbed ionic species of oxygen; react most effectively with gas molecules at this particular temperature, on the film surface [25].

Finally, the obtained results indicate that the sensor material, $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ nanocrystalline film, do release the adsorbed gas during heating up to 180°C, while the material adsorbs the environmental gas, e.g. H_2 , during cooling to room temperature [5]. This result may suggest that this material is able to act as hydrogen, petroleum and humidity sensor during the heating and cooling process.

V. CONCLUSION

Nanocrystalline $\text{Na}_{0.1}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ thin film was used as a gas sensor. The thin film was deposited on a glass substrate via the sol gel technique. Hydrogen, petroleum and humidity gas-sensing properties were examined and compared with each other. The size of the nanocrystals was found to be about 7.5 nm applying XRD and TEM. At low temperature for different gasses the maximum sensitivity is 0.85 in the operating temperature range of 40–80°C for heating and cooling period. At high temperature for different gases, the sensitivity is maximum i.e. 0.6-0.85 at 130-150°C operating temperature. The maximum response is attributed to the availability of sufficient adsorbed ionic species of oxygen; react most effectively with gas molecules at this particular temperature, on the film surface.

ACKNOWLEDGMENT

The authors would like to acknowledge the support of the Ministry of Higher Education, Kingdom of Saudi Arabia for supporting this research through a grant (PCSED-018-12) under the Promising Centre for Sensors and Electronic Devices (PCSED) at Najran University, Kingdom of Saudi Arabia.

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