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Abstract

In this work, vanadium pentoxide (V_2O_5) thin film was synthesized on the corning glass substrate by using thermal evaporation method. For this purpose, 99.9% pure V_2O_5 powder was used that was evaporated from a tungsten boat. Subsequently, the prepared film was used as pH sensor in the extended gate field-effect transistor (EGFET) system. Structural properties, morphological features, sensing performance and linearity measurements of synthesized film were studied. The structural properties indicated that the V_2O_5 thin film has the preferred orientation along (001) plane. The pH-EGFET sensor based on V_2O_5 thin film was fabricated. The sensitivity and linearity of the device were determined in the pH range of 2–12 of the buffer solution. The sensitivity and linearity values were found to be 41.7 mV pH^{-1} and 83% respectively in the linear region. The results of present study show that the V_2O_5 can act as promising material for the EGFET PH sensor.

1. Introduction

The extended gate field-effect transistor pH sensing has been applied and developed in promising numerous fields such as environmental detections, biosensor application, clinical measurements, and analytical chemistry [1, 2]. Since Bergveld [3] proposed the field effect transistor for ion sensitive (ISFET) in 1970, several studies have worked to enhance the detecting properties of the ISFET [4]. ISFET developed a various structure denoted to as extended gate field-effect transistor system, that is low-cost, flexible shape, simpler package, and long stability as compared to the ISFET [5]. Several metal-oxide based thin films have been utilized as a membrane of the pH sensor such as tin oxide [6], titanium oxide [7], and zinc oxide [8]. Among these, vanadium pentoxide (V_2O_5) can be utilized for pH sensor device due to its excellent electrical, high conductivity, and stability. Guerra *et al* [9] synthesized V_2O_5 film on glassy carbon as a pH-EGFET sensor using sol-gel method. This substrate is a non-graphitizing, carbon which combines glassy and ceramic properties with those of graphite. The pH sensor device showed linear response to the various buffer pH solutions. This film revealed a good linearity and sensitivity within the pH values 2–12 of sensitivity 58.1 mV pH^{-1}. The results shown that the pH 12 cannot be not utilized in the sensing measurement as the V_2O_5 xerogel is unstable at pH 12, which was attributed to the production of met-avanadate in the solution [10]. Guidelli *et al* [11] evaluated V_2O_5/WO_3 film using sol-gel method on glassy carbon substrate. The V_2O_5/WO_3 gel was obtained from 0.1 M $NaWO_3$ (sodium tungstate) and 0.1 M $NaVO_3$ (sodium meta-vanadate) via using ion exchange technique. The acid solution was prepared via the filtrating procedure through a cationic ion-exchange resin at pH 3. The final solution was contained 5% WO_3 and 95% V_2O_5 percentages, which was kept for two weeks at room temperature. The reaction was generated a viscous red V_2O_5/WO_3 gel. In order to the best response, V_2O_5 was mixed with a molar concentration of 5% WO_3, which was operated linearly performance even in case of the pH value up to pH 12.

The good results can be attributed to the layered structure of V_2O_5, which intercalates a large number of the organic and inorganic species. This produces a stable of the electronic properties which attributes to the surface diffusion of the ions (H^+) in the aquatic phase. Thin film membrane was tested as a pH sensitivity of 1.36 $\mu A^{1/2}$ /pH in saturation regime, and linear sensitivity of 68 mV pH^{-1}. Vieira *et al* [12] used V_2O_5 nanostructures as pH-EGFET sensor application. The results indicated that the sensitivity of the sensor was close with the theoretical limit value 59.2 mV pH^{-1} as compared with other nanostructure membranes. Several of the researchers studied the sensing application of the V_2O_5 thin film as pH-EGFET [9, 11]. On the basis of previous studies, there is no relevant study published for V_2O_5/Corning glass thin films as pH-EGFET sensor by using thermal evaporation method. In this current study, V_2O_5 thin film membrane was synthesized on the corning glass substrate using thermal evaporation technique. Afterward, the deposited thin film membrane used as a pH-EGFET sensor application. The results indicated good sensitivity and linearity, which relates to the sensing large areas of the thin film.

2. Experimental

2.1. V_2O_5 thin film preparation

V_2O_5 thin film membrane was deposited on corning glass substrates in a vacuum chamber by using thermal evaporation technique. The source material V_2O_5 (purity 99.997%) was evaporated from the tungsten small boat. The chamber pressure of the deposition method was maintained at 5×10^{-6} mbar. The distance between the source material and the substrate was fixed at 35 cm. The thermal annealing process was achieved by using furnace system (Nabertherm model R 120/1000) with a changing the temperature annealing from 100 °C to 500 °C under air pressure conditions.

2.2. Characterization techniques

The structural properties were investigated through HR-x-ray X'Pert PRO MRD PW 3040 from the PANalytical x-ray diffractometer system equipped with Cu-K radiation ($\lambda = 1.54056$ A°), which operates at 40 kV and 30 mA and Raman spectrometer system (Horiba Jobin Yuon HR 800UV, Edi-son, NJ, USA) with Ar+ as the excitation source operated at a wavelength of 514.55 nm (20 mW). The surface morphology was studied by using field emission scanning electron microscopy (FESEM) (model FEI Nova NanoSEM 450) equipped with energy dispersive x-ray spectrometer (EDX) for chemical components. The sensitivity measurements of V_2O_5 thin film membrane was examined using Keithley (2400) high voltage source and MOSFET (HEF4007UBD) system.

2.3. pH-EGFET sensor fabrication

The pH-EGFET sensor based on V_2O_5 thin film was fabricated. In this regard, the sample was connected with the membrane cavity to collect the reference electrode with the sample in different pH solutions. During the measurement process, the temperature was controlled to prevent the effects on the pH solutions and electrical properties of the MOSFET ((HEF4007UBD) system. Subsequently, the reference electrode was attached to the sensing area (1×1 cm^2) of the glass substrate. The measurement was performed using various pH solutions of range 2–12. The measurements of drain current to drain voltage (I_{DS}-V_{DS}) and drain current to reference voltage (I_{DS}–V_{RFF}) were made using two Keithley (2400), as revealed in the figure 1.

3. Results and discussion

3.1. Structural characteristics of the V_2O_5 thin film

The diffraction peaks of V_2O_5 film prepared on corning glass substrate using thermal evaporation method are shown in figure 2. The results indicate the diffraction peaks of V_2O_5 along various planes. The diffraction peak at $2\theta = 20.1°$ is associated to plane (001) with high intensity. The XRD peaks at (101), (110), (301), (011), (002), (020) reflections are indexed with the orthorhombic crystal structure. These peaks were matched to the standard list of the V_2O_5 thin film (JCPDS Card No. 00–041–1426) [13]. After the films' annealing, the XRD peaks become sharp and larger in intensity due to improvement in the crystallinity of V_2O_5 thin film [14]. These results are in agreement with previous studies such as Akl *et al* [15], Vijayakumar *et al* [16], Santos *et al* [17] and Kumar *et al* [18]. However, Guerra *et al* [9] found different results as compared with the current work whose detail has been presented in the introduction section. The crystallite size 'D' of V_2O_5 thin film membrane along the high intensity peak (001) has been calculated using Debye Sherrer's formula [19]:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \tag{1}$$

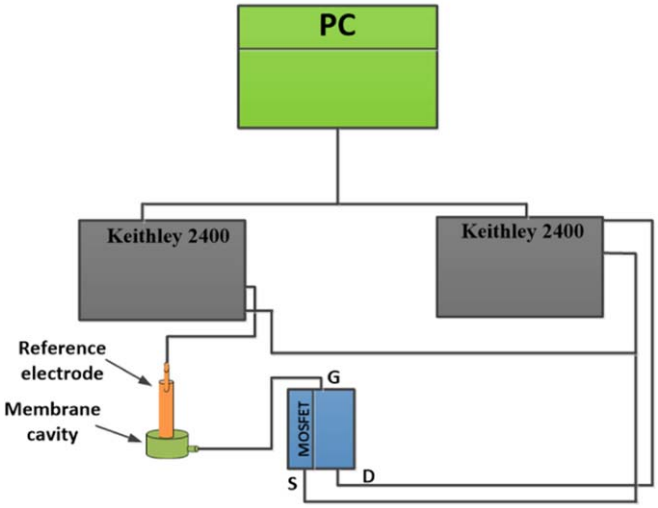

Figure 1. Schematic diagram of pH-EGFET sensor based on V_2O_5 thin film membrane.

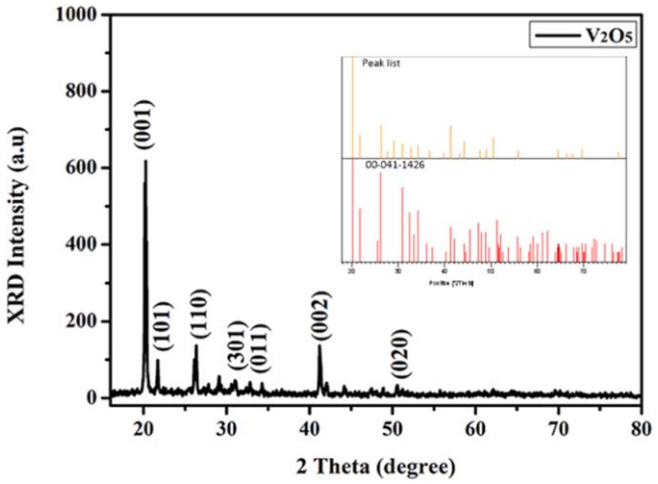

Figure 2. XRD patterns of the V_2O_5 thin film deposited on the glass substrate.

Here, λ is the incident wave-length of the XRD radiation (1.5406 Å), β is represents to the full-width half maximum (FWHM), θ is the angle of the XRD diffraction. The crystallite size value along (001) peak has been found to be 26.5 nm.

The strain behaviour was calculated of the V_2O_5 thin film along (001) peak using the relation:

$$\varepsilon_{zz} = \frac{c - c_o}{c_o} \tag{2}$$

where c is represents to the lattice constant of the V_2O_5 film, c_o is the standard lattice constant, which estimates from the XRD measurements. The strain value has been found to be 0.228%. The value indicates the tensile behaviour of the V_2O_5 thin film.

Figure 3 indicates the Raman bands of the deposited V_2O_5 thin film that were examined in the range 100–1000 cm^{-1}. The Raman peaks are associated to the orthorhombic structure of the V_2O_5 thin film [20]. These result are also in agreement with the previous investigations [21]. The high intensity of the Raman spectra peak centred at B_{3g} mode (143 cm^{-1}) can be related to the lattice structure vibrations. This peak is attributed to the vibration of V–O–V mode and this validates the orthorhombic structure of V_2O_5 thin film [22]. The Raman peak at (195 cm^{-1}) is associated to the layered structure [23]. The peak located at 992 cm^{-1} could be attributed to A_g mode of terminal oxygen band (V=O). The observed peak at 695 cm^{-1} is associated to the stretching mode (V_2–O) which is attributed to the two pyramids from corner-shared oxygen atoms. Two Raman peaks located at 480 cm^{-1} and 303 cm^{-1} occur due to the stretching vibrations of V–O–V and V_3–O bands, respectively. The Raman peaks positioned at 282 cm^{-1}, 404 cm^{-1} are related to the V–O bands from the bending modes [24].

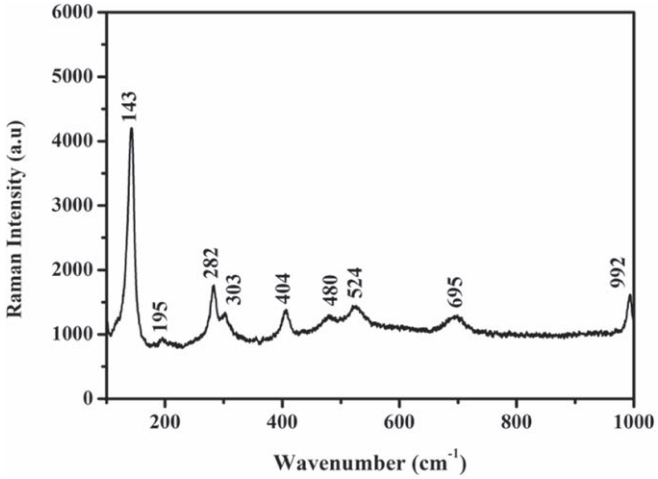

Figure 3. Raman spectra of V_2O_5 thin film membrane deposited on corning glass substrate.

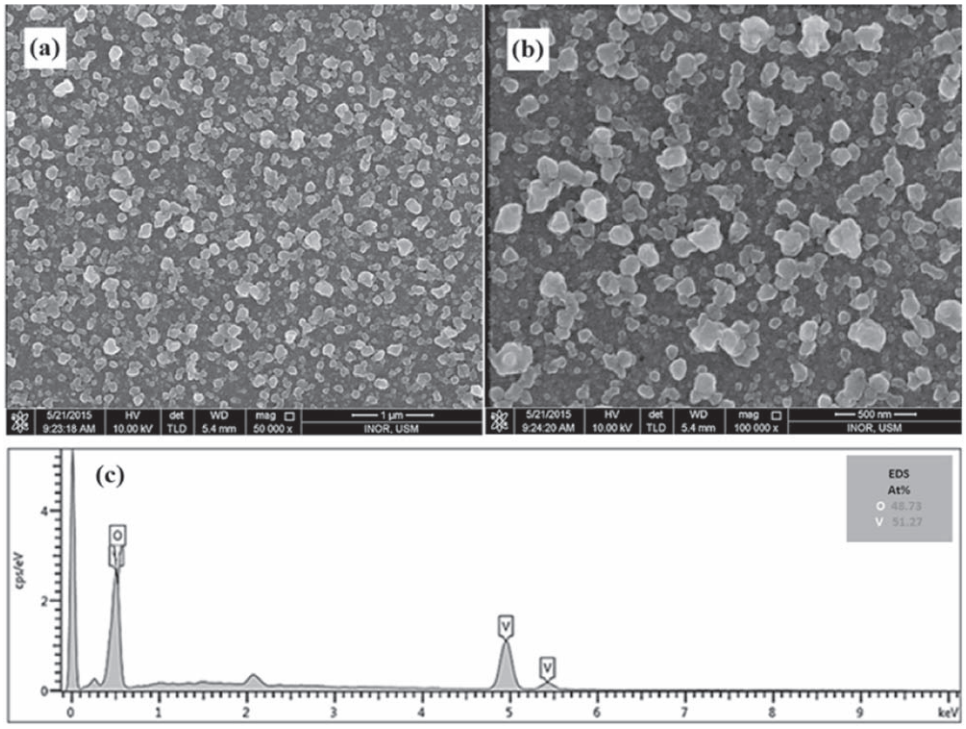

Figure 4. FESEM images of the V_2O_5 thin film (a) magnification (1 μm) (b) magnification (500 nm) (c) EDX spectra of V_2O_5 thin film membrane deposited on glass substrate.

3.2. Morphological characteristics of the V_2O_5 thin film

The morphological characteristics of V_2O_5 thin film membrane was examined through FESEM and the corresponding images are shown in figure 4. The images show the formation of uniform and smooth films. The grain size varies between 80 nm and 150 nm. Furthermore, films contain dense and compact grains along with good adherence to the surface. The films formed are homogenous without agglomerations on the surface. Figure 4(c) shows the EDS spectrum of V_2O_5 thin film. The results indicated that the film contains high purity without any contamination. The film contains 51.27 wt% V, 48.73 wt% O which is close with the chemical composition of the V_2O_5 material.

3.3. Performance of V_2O_5 thin film as pH sensor

The pH-EGFE sensor based on the V_2O_5 thin film membrane is shown in figure 5. The pH sensitivity and linearity of the sensor were examined in various buffer solutions (pH $=$ 2, 4, 6, 8, 10, 12), with the sensing area of

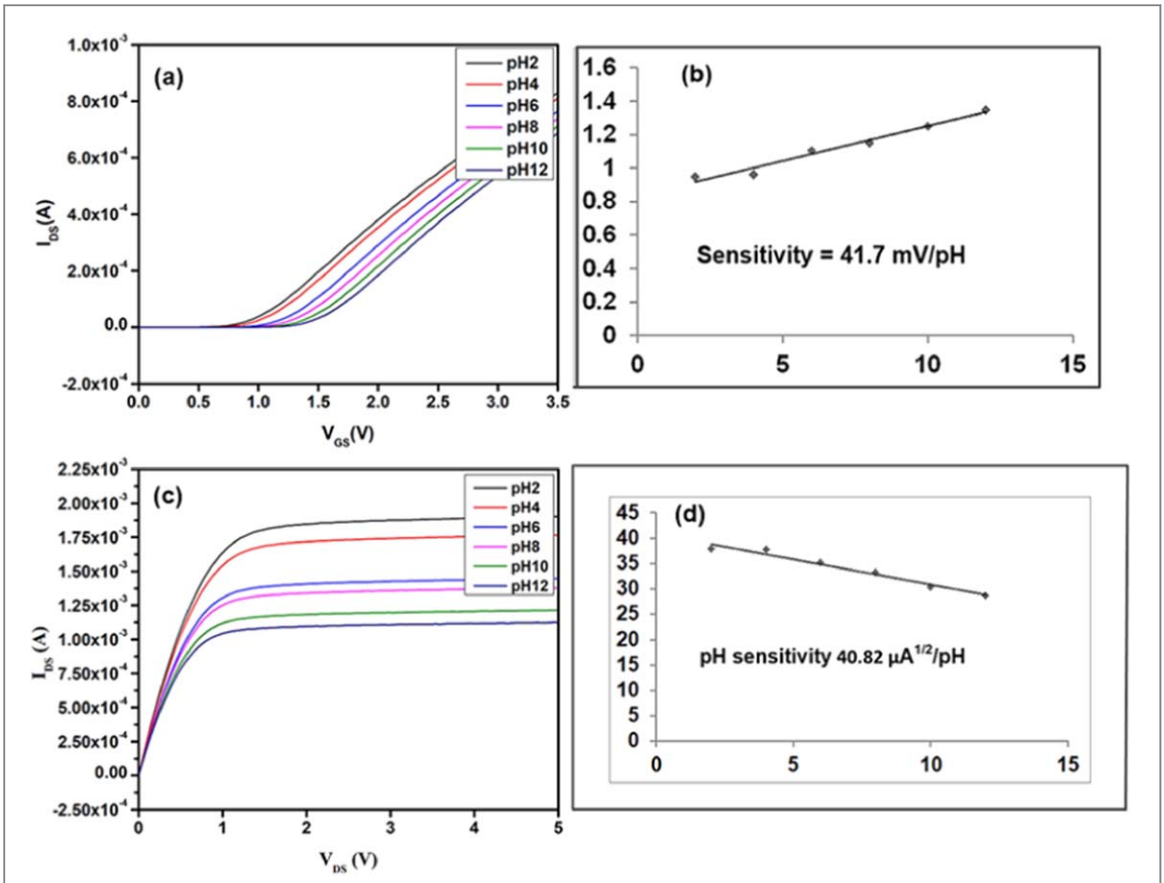

Figure 5. pH-EGFET sensor based on V_2O_5 thin film (a) I_{DS}–V_{GS} characteristics (b) sensitivity in the linear region (c) I_{DS}–V_{DS} characteristics (d) sensitivity in the saturation region.

1 cm^2 surrounded the ring diameter. The linear region was carried out at 0.3 V of the voltage (drain-source), the saturation region was carried out at 3 V of voltage (gate-source), as shown in figures 5(a)–(c). The results show that the curves of the threshold voltages change to the right side with decreasing hydrogen ions numbers. Furthermore, the drain current decreased with increasing the pH values; i.e. decreasing of hadron ions numbers. These results reveal a good performance of V_2O_5 film membrane as compared to the previous membranes prepared via different methods [9, 11]. For the linear region, the sensitivity value of the pH sensor was evaluated from the line slope, which was 41.7 mV pH^{-1} and the linearity value was found to be 83%, respectively. The sensitivity of pH at saturation region of the V_2O_5 film membrane was 40.82 $\mu A^{1/2}$ /pH and the linearity value was 99%, respectively. The fast sensor response of the membrane is commonly associated to the chemical reactions at the external surface layers. Since the area and shape of thin film was kept constant, the increment in the oxide volume indicates in the augmentation of the oxide layers number constituting the thin film and, consequently, the increase of deprotonation sites number in the bulk, which leads to fast sensor response. The results indicate that the V_2O_5 membrane shows good performance and is stable at pH 12 as compare to that investigated in the past studies [11, 25]. The sensitivity can be attributed to the conductivity of the thin film [11]. For this study, the pH sensitivity of V_2O_5 membrane is related to the crystalline structure and effective sensing area, which was an important role in the improvement of sensitivity [26]. In addition, the sensing area and the sites numbers on the membrane surface show control pH sensing. Therefore, the pH sensing is dependent on site reactions of the external surface, which increases the surface potential of thin film membrane. This increases the aggregation of the electrical positive charges on the membrane surface and enhances the pH sensitivity. This indicates that the V_2O_5 membrane synthesized on corning glass by thermal evaporation method is a good potential pH-EGFET material for application as a pH sensor with excellent linearity. The parameter (β) of the sensitivity can be measured by using equation below [27]:

$$\beta = \frac{2q^2N_s\sqrt{\left(\frac{K_a}{K_b}\right)}}{kTC_{DL}} \tag{3}$$

where q is represents the charge of electrons, N_s denotes to the density of the surface sites, K_b and K_a denotes to the basic and acidic equilibrium constants, k is defined as Boltzmann factor, C_{DL} symbolizes the capacitance of

double layer according to the Gouy-Chapman theory [28]. The mechanism of the surface charge has been described using the site-dissociation theory. The interaction theory between the membrane surface and connected electrolytes is assumed to the isolated reaction sites on the membrane surface, which is susceptible to dissociation process. The insulator surface consists of hydroxyl groups (MOH), which represents positively charged depending on the (H^+) ions concentration in the solution. After the solution matches the surface of the film, hydroxide groups (MOH) act as separate sites for chemical reactions in the thin film. This sensing mechanism starts with the accepting or donating of the proton (H^+) to form positive or negative ions in the solution, respectively.

The pH of the solution activates the hydroxide ions to bind with the proton (MOH_2^+) or discharge a proton (MO^-), which are the binding sites. The exchange reaction of proton is dependent on the concentration and distribution of the solution over the membrane surface, type of the surface sites and material, in addition to the point of zero charge (pH_{pzc}) (i.e. the point that the density of the surface charge is zero) [29]. The voltage of the surface potential between electrolyte solution interface and sensing surface is expressed as below following [30]:

$$\psi = 2.303\frac{kT}{q}\frac{\beta}{\beta+1}(pH_{PZC} - pH) \tag{4}$$

The mechanism of the reaction between membrane surface and electrolyte solution with the different pH values can be explained as, when pH $>$ pH_{pzc} then the hydroxide groups on the surface provide (OH^+), and when pH $<$ pH_{pzc} then the hydroxide gives (O^-). If pH $=$ pH_{pzc} then it indicates a neutral charge (OH), as given below [11];

$$M - OH_2^+,\ M - OH + H^+,\ M - O^- + 2H^+$$

According to this mechanism, the surface of the membrane will be charged negative or positive voltage which conducts to the MOSFET system. When positive voltage is applied, the conduction channel will increase, leading to increased sensitivity. Conversely, the conduction channel will decrease, resulting in decreased of the sensitivity. The pH sensitivity value is considered acceptable as compared to the lower sensitivities, but can be enhanced by modifying numerous essential factors, such as the methods of preparation, substrate type, and measurement conditions.

4. Conclusion

V_2O_5 thin film membrane as pH sensor was synthesized on the corning glass substrate by using thermal evaporation technique. The structural, morphological characteristics of thin film membrane were examined via using XRD diffraction, Raman spectroscopy, and FESEM system. The pH sensitivity and linearity of the membrane were studied using reference electrode and MOSFET (HEF4007UBD) instrument. The results indicated that the V_2O_5 thin film exhibits a sensitivity and linearity in the linear region whose values are found to be 41.7 mV pH^{-1} and 83%, respectively. The sensitivity value and linearity in the saturation region are 40.82 $\mu A^{1/2}$ /pH, and 99%, respectively. These results can be assigned to the large surface area of the thin film which increases the number of the surface sites, resulting in an increase in the pH sensitivity.

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