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Effects of Annealing on the Structural and Optical Properties of V_2O_5 Thin Films Prepared by RF Sputtering for Humidity Sensor Application

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Abstract

In this work, vanadium pentoxide (V2O5) thin films were prepared using rf magnetron sputtering on silicon wafer and glass substrates from V2O5 target at 200 °C substrate temperature, followed by annealing at 400 and 500 °C in air for 2 h. The prepared thin films were examined by X-ray diffraction (XRD), forier transform infra-red spectroscopy (FTIR), UV-visible absorbance, and direct current coductivity to study the effects of annealing temperature on their structural and optical properties. The XRD analysis exhibited that the annealing promoted the highly crystallized V2O5 phase that is highly orientated along the c direction. The crystalline size increased from 22.5 nm to 35.4 nm with increasing the annealing temperature to 500 °C. The FTIR spectroscopy showed the enhancement of the characteristics band for the V2O5 with increasing annealing temperature to 500 °C. The optical study showed that the energy gap for the sample deposited on glass slides decreased from 2.85 eV, for as deposited sample, to 2.6 eV upon annealing the sample to 500 °C. There was a linear dependence between sensitivity and relative humidity (RH) at the range from 25% to 70%, while the behavior was exponential at high RH range.

Keywords: vanadium oxide, rf sputtering, FTIR

تأثير التلدين على الخصائص التركيبية والبصرية للأغشية الرقيقة V2O5 المُعدّة بطريقة الترذيذ بالتردد الراديوي لتطبيق مستشعر الرطوبة

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الخلاصه

في هذا العمل ، تم تحضير أغشية رقيقة من خامس أكسيد الفاناديوم (V_2O_5) باستخدام الترسيب التردد الراديوي rf على رقاقة السيليكون والركائز الزجاجية من الهدف V_2O_5عند درجة حرارة ركيزة 200 درجة مئوية ، متبوعًا بالتلدين عند 400 و 500 درجة مئوية في الهواء لمدة ساعتين. تم فحص الأغشية الرقيقة المحضرة بتقنيات مختلفة لدراسة تأثير درجة حرارة التلدين على خواصها التركيبية والبصرية. يُظهر حيود الأشعة السينية (XRD) التلدين يعزز طور V_2O_5عالي التبلور ذي التوجيه العالي على طول اتجاه .c يزداد الحجم البلوري من 22.5 نانومتر إلى 35.4 نانومتر مع زيادة درجة حرارة التلدين إلى 500 درجة مئوية. يُظهر التحليل الطيفي FTIR تحسين نطاق خصائص V_2O_5مع زيادة درجة حرارة التلدين إلى 500 درجة مئوية. أظهرت الدراسة البصرية أن فجوة الطاقة للعينة المودعة على الشرائح الزجاجية تقل من 2.85

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eV ، للعينة المودعة ، إلى 2.6 eV عند التلدين إلى 500 درجة مئوية. تعتمد البطانة على الحساسية مع الرطوبة النسبية في نطاق من 25٪ إلى 70٪ ، بينما السلوك الأسي في نطاق رطوبة نسبية مرتفع.

1. Introduction

The humidity affects all environmental biological and chemical processes. It also negatively affects various industrial-manufacturing methods if proper steps are not taken [1]. Humidity sensors determine the amount of water vapor present in air [2]. Different materials have been used as active substances for humidity sensing, such as ceramic oxides or composite oxides of semiconductors [3]. H_2O is adsorbed on oxide surfaces in molecular and hydroxyl forms, leading to increase their conductivity [4]. Plasma sputtering deposition is of great importance in the fields of industry and technology because of the distinct properties of the prepared thin films, such as homogeneity and purity [5]. Vanadium oxide (V_2O_5) is a promising substance that is used in energy storage and photovoltaic applications [6]. It is an n-type of the highest oxidation phase and the highest stable than other vanadium oxide phases [7]. The structure of the V_2O_5 belongs to the pmnm space group with unit cell dimensions of a =11.510 Å, b=4.369 Å, c = 3.563 Å. The structure is installed from a deformed trigonal bipyramidal coordination of O around V, which shares edges to compose zigzag double chains along the z-direction and is cross-linked along x-direction by shared corners, forming sheets in the x-z plane [8].

V_2O_5 exhibits interesting structural, optical, and electrochemical properties [9], including multi-valance, layered structure, broad optical energy gap (2.44 eV), perfect chemical and thermic stabilization, and excellent thermoelectric properties . V_2O_5 is a promising material for the development of numerous semiconductor devices, such as sensors and optical-electrical switches [10].

V_2O_5 is processed in a thin film configuration to develop electrical and optical devices. The deposition technique and the precipitation parameters, such as deposition rate, substrate temperature, sputtering power, and pressure, determine the thin film properties. In interactive sputtering, the processed gases, such as oxygen, are added with the inert working gases, such as argon. The major advantage of DC sputtering lies in high deposition rate, whereas in the case of rf sputtering, various types of targets can be used, such as semiconductors and insulators [11].

In this paper, the effects of annealing temperature on the structural and optical properties of V_2O_5 thin films was studied by using radio frequency sputtering technique on Si and glass substrates. We employed the deposited V_2O_5 thin film in the development of resistive type humidity sensors by studying the variation in sample resistance versus relative humidity.

2. Experimental part

Vanadium pentoxide powder with a purity of 99.99% (Torr International Inc., New York, USA) was compressed by a hydraulic piston in mold to prepare a disk of 5 cm diameter and 5 mm thickness, which was sintered at 500 °C for 4 hours and installed in the magnetron gun as a sputtering target. Compact Research Coater System (CRC-600; Torr International Services LLC) of stainless steel chamber was vacuumed by a rotary and turbo-molecular pump to 10^{-6} Torr base pressure. Silicon and glass slide substrates were cleaned chemically, by distilled water and alcohol, and ultrasonically and dried using electric oven at 60°C. Thin films were prepared using planar magnetron sputtering source by RF power supply with rotational substrate controller at 200 °C. The inter-electrodes spacing is equal to 4cm. Oxygen and argon gases were delivered to the system by a gas flow controller at 10% mixing ratio. Thin films were deposited using 150 Watt rf power at 1×10^{-2} Torr pressure. The final samples were annealed at 400 and 500 °C temperatures for 2 hours in air.

X-ray diffraction system (D2 PHASER, Bruker, Germany) was used to characterize the crystalline structure of the prepared samples at diffraction angle range (2θ = 20°- 60°). FTIR spectrometer (Shimadzu FTIR-8400S) from LABX was used to study the chemical bands.

Optical measurements of thin films were performed by UV-Visible spectrometer (UV-vis Shimadzu 1700) for samples deposited on glass slide. Film thickness was determined by using TFProbe TM from Angstrom Sun Technology Inc. and found to be about 200 nm.

The electrodes of 3 mm width and 1 mm separation were printed on the sample surface using silver paste by print screen. D.C electrical measurements were conducted at a temperature range of 298 to 473 K in electrical furnace using PC-interfaced digital multimeter (Vector70C) connected with personal computer.

The humidity sensor, based on resistance variation, was built using V_2O_5 thin film deposited on Si substrate and annealed at 500 °C. Silver paste was used to deposit mesh electrodes on the surface of V_2O_5 by print screen and dried in an oven at 70 °C. After that, silver paste was used to connect the thin wire in the two terminals. The sample was placed in a homemade controlled humidity chamber, which consists of a nebulizer with controlled valves and temperature. The relative humidity was monitored by a standard hygrometer. The variation of sample resistance was measured under dark conditions using an electronic circuit connected with computer. The RH varied from approximately 25 to 90 %, using moisture generator.

3. Results and discussion

The X-ray diffraction patterns for vanadium oxide thin film prepared by rf sputtering plasma on (100) silicon substrate at 200 °C and annealed at 400 and 500 °C are shown in Figure 1. Low crystalline as-deposited film with a broad peak appeared at 19.92 ° diffraction angle (2θ), corresponding to (001) for V_2O_5, referring to JCPDS standard card No. 96-901-2222. Annealing of the sample at 400 °C enhanced its crystallinety and the sample appeared as a pure V_2O_5 phase of polycrystalline structure with five peaks located at $2\theta = 15.08^0$, 19.90^0, 30.50^0, 40.40^0 and 46.64^0, consistent with (200), (001), (400), (002), and (600) crystal planes, respectively. The crystalline film appeared with high orientation along the (001) direction, which agrees with the results reported by Raman *et al*, [12]. More crystalline enhancement was observed when the sample was annealed at 500 °C temperature.

The mean peaks profile was characterized by Lorentzian fitting, as shown in the inset figure, to find the peaks width at half maximum. It seems that the peaks breadth decreased with increasing the annealing temperature, i.e. increase in crystalline size.

Detailed values of the diffraction angles (2θ), the full width at half maximum (FWHM), the inter-distance (d_{hkl}) calculated by the Bragg's law for the crystalline planes with Miller indices (h, k, l), and the crystalline size (C.S) calculated by the Sherrer's formula are listed in Table 1.

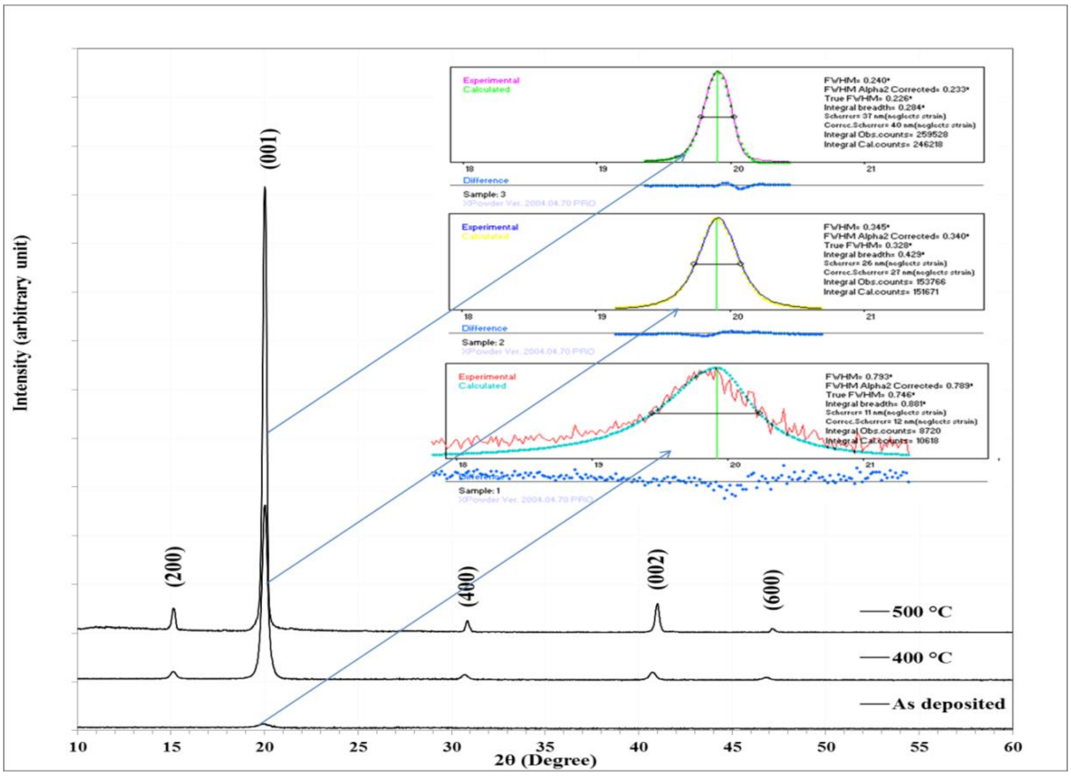

Figure 1- XRD spectra for V_2O_5 thin film annealed at different temperatures.

Table 1- XRD peak parameters for V_2O_5 thin film annealed at different temperatures.

Annealing (°C)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	C.S (nm)	hkl
As deposited	19.92	0.7930	4.4536	10.2	(001)
400	15.08	0.3569	5.8704	22.5	(200)
	19.90	0.3452	4.4580	23.4	(001)
	30.50	0.3848	2.9285	21.4	(400)
	40.40	0.4120	2.2308	20.5	(002)
	46.64	0.4418	1.9562	19.6	(600)
500	15.08	0.2262	5.8704	35.4	(200)
	19.95	0.2402	4.4470	33.6	(001)
	30.62	0.2306	2.9173	35.7	(400)
	40.66	0.2684	2.2172	31.6	(002)
	46.98	0.2813	1.9419	30.8	(600)

Figure 2 shows the FTIR spectra for the prepared thin films at different annealing temperatures. The V_2O_5 structure is combined from the bonded VO_5 trigonals in zigzag chains. Each VO5 group contains a short V=O bond, as shown by Bachman *et.al*. [8]. Typical bands of crystalline V_2O_5 structure appeared especially at 500 °C annealing temperature, where the band around 1034-1072 cm^{-1} is assigned to the V=O bond. The band around 876-883 cm^{-1} corresponds to symmetric stretching vibrations along V-O-V chains involved in corner sharing of VO5 polyhedra [13], while the peak present around 610- 617 cm^{-1} refers to bending mode vibrations of V-O-V bond [13]. The band around 459- 468 cm^{-1} is ascribed to the vibration band of the V-O bond [14]. The observed V_2O_5 bands are consistent with those reported before [15, 16]. These bands were obviously enhanced at 500 °C. The broadening of V=O peak is possibly due to a slight change in the length of the bond.

The V=O band vibration occurs towards lower wave number, while that of the V-O-V band occurs toward higher wave number, proposedly due to variations in bonds length which are attributed to strain and stress effects with crystalline size changes [14]. The enhancement of band intensity at 1034 cm^{-1} relative to the other bands indicates the enhancement of V_2O_5 structure, as shown by increasing it's crystalline in XRD measurement. Other peaks appeared in the FTIR curves, which are due to the gas molecules adsorbed from the atmosphere on the sample surface. The FTIR bands that appeared in the three patterns are illustrated in Table 2.

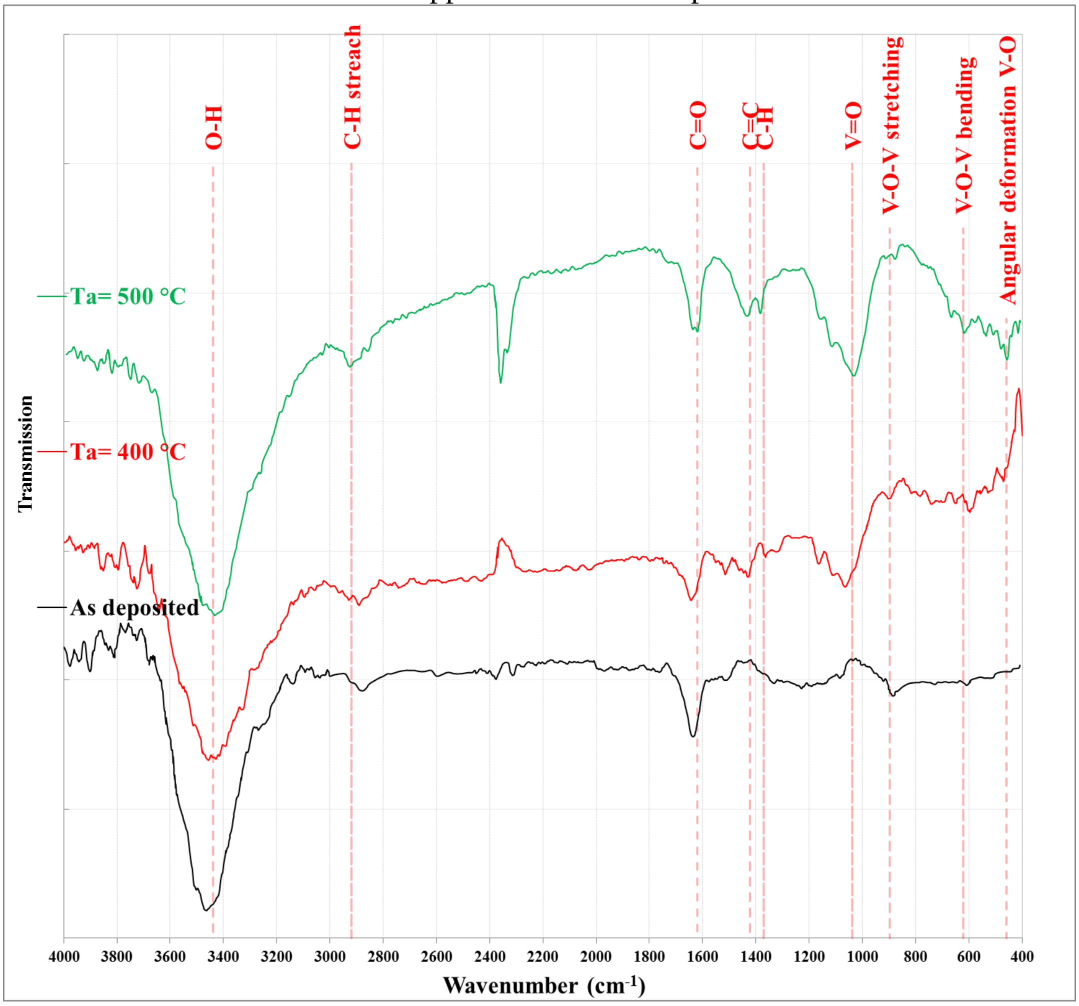

Figure 2-FTIR spectra for the vanadium oxide thin film annealed at different temperatures.

Table 2- FTIR bands in cm^{-1} for the vanadium oxid thin film annealed at different temperatures.

Bond type	**Annealing temperature (°C)**		
	As deposited	**400**	**500**
O-H	3463.83	3438.30	3434.04
C-H stretch	2885.11	2893.62	2923.40
C=C	1638.30	1642.55	1621.28
	1434.04	1429.79	1434.04
C-H bend	1336.17	1361.70	1382.98
V=O	1072.34	1063.83	1034.04
V-O-V stretching	883.36	897.87	876.60
V-O-V bending	610.76	611.50	617.02
Angular deformation V-O	-	468.09	459.57

The energy gap of the prepared and annealed vanadium oxide thin films, at different temperatures, was measured using a UV-visible absorption spectrum using the Tauc formula, as illustrated in Figure 3. The energy gap of the as-deposited thin film was 2.85 eV, which is greater than that reported by a previous study, which was 2.4 eV [17]. This is due to the quantum confinement effect, which occurs when the sample particle size is in the nano-scale. The absorption edge appears to shift towards the long wavelength and be sharper after annealing the sample, especially at a temperature of 500 °C. This effect is due to the reduction of the tails energy near the energy band edge, which is caused by the enhancement of crystalline growth and the reduction of crystal defects after annealing. Increasing annealing temperature caused a decrease in the optical energy gap to 2.6 eV, which can be due to increasing crystalline size.

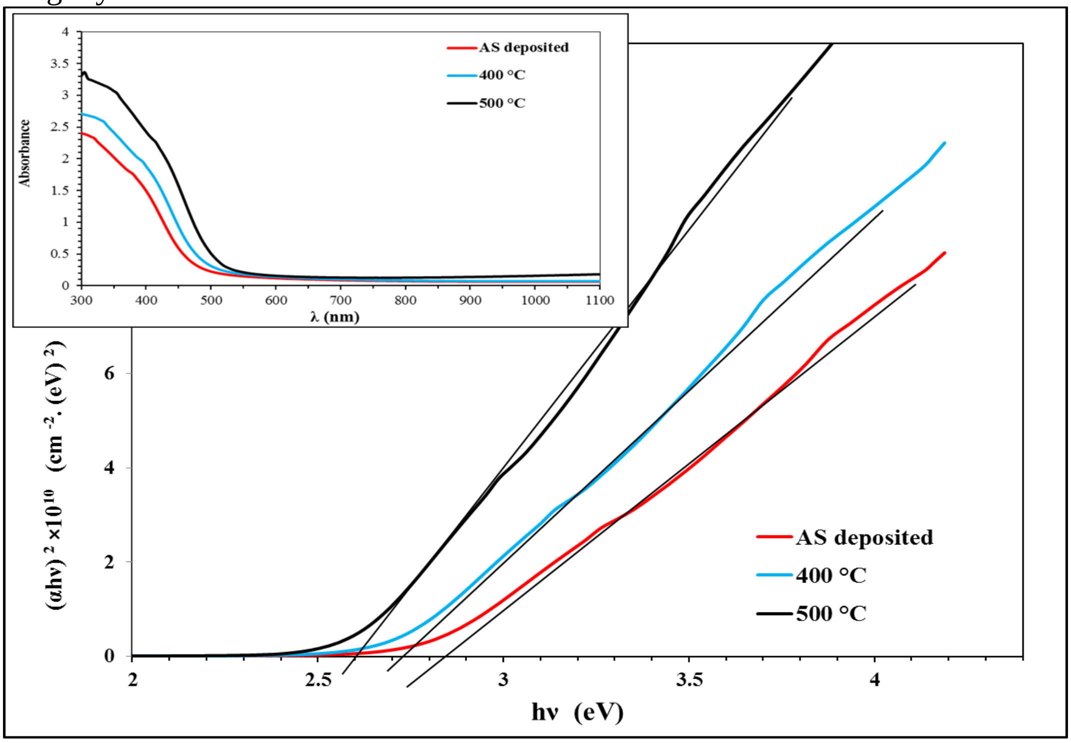

Figure 3-Energy gap values for V_2O_5 thin films at different annealing temperatures using Tauc relation.

The semiconductor conductivity obeys the formula $\sigma = \sigma_\circ e^{-E_a/KT}$, where $\sigma_\circ$ is a pre-exponential factor and E_a is the activation energy, which can be determined from the slope of linear relation between $\ln(\sigma)$ and reciprocal of temperature, as shown in Figure 4, for the V_2O_5 prepared at different substrate temperatures. The conductivity increase with increasing substrate temperature, as a result of increasing charge carrier mobility with increasing thin film crystallinety and reducing defects therefore the trap sites. Each sample has two activation energies, which decrease with increasing annealing temperature. Table 3 shows the calculated values of conductivity at room temperature (RT) and activation energies.

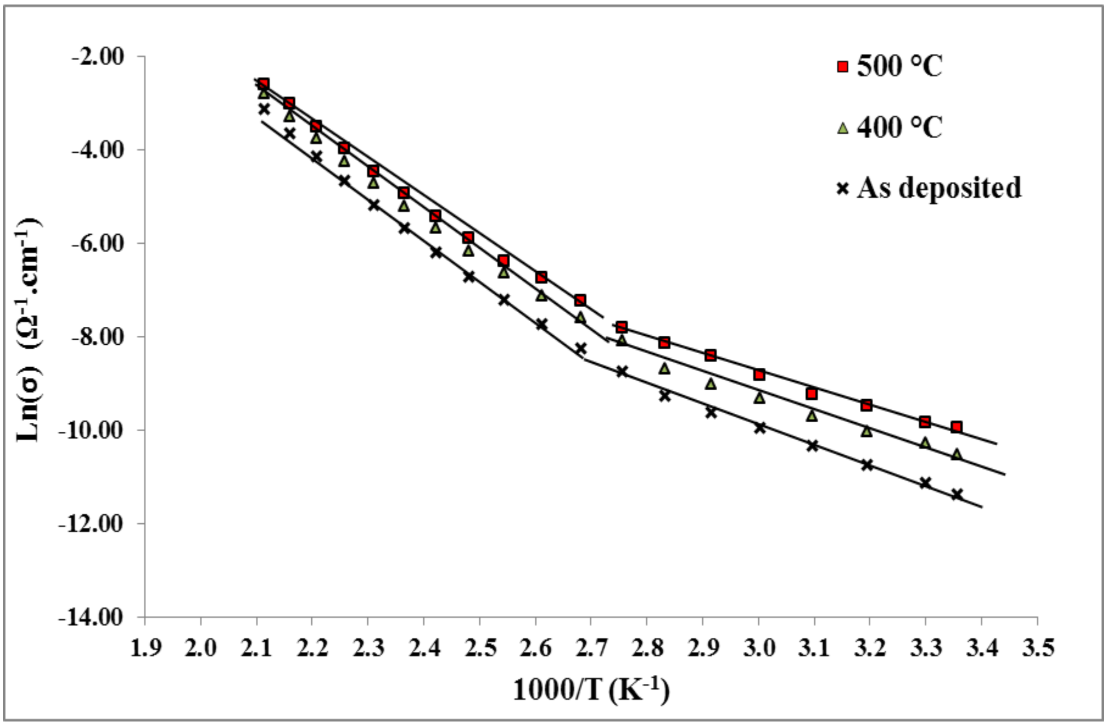

Figure 4- Logarithm of conductivity vs. reciprocal temperature for the V_2O_5 thin films.

Table 3- Activation energies and direct current conductivity at RT for the V_2O_5 thin films.

Annealing Temp. (°C)	E_{a1} (eV)	E_{a2} (eV)	σ_{RT} ($\Omega^{-1}.cm^{-1}$)
As deposited	0.361	0.7563	1.1E-05
400	0.327	0.7080	2.7E-05
500	0.313	0.6964	4.7E-05

Humidity is measured as the ratio of water vapors pressure in air to the saturated pressure of water vapor at this temperature, which is called relative humidity (RH). The sensing layer, used as a dielectric layer, absorbs and desorbs water molecules, proportional to RH present in the ambient air, and accordingly changes the sensor resistance. Figure 5 (a) shows the resistance variation for V_2O_5-based sensors, deposited by rf sputtering and annealed at 500 °C, with time, under different RH values (25–90%) at RT (30 °C). Figure 5 (b) shows the variation of sample resistance with RH for the V_2O_5 resistive humidity sensor. This curve shows good linear behavior at the range from 25 to 70% RH, where the resistance decreases from 52 to 37 MΩ with increasing humidity levels at this range. It can also be seen that the resistance variation at high humidity presents nonlinearity with RH, which could be attributed to different conductivity mechanisms. V_2O_5 exhibits both electronic and ionic conductivities. A similar observation was also noticed by Karimov *et al*. [17]. Figure 5 (c) displays the variation of sensitivity with the value of RH.

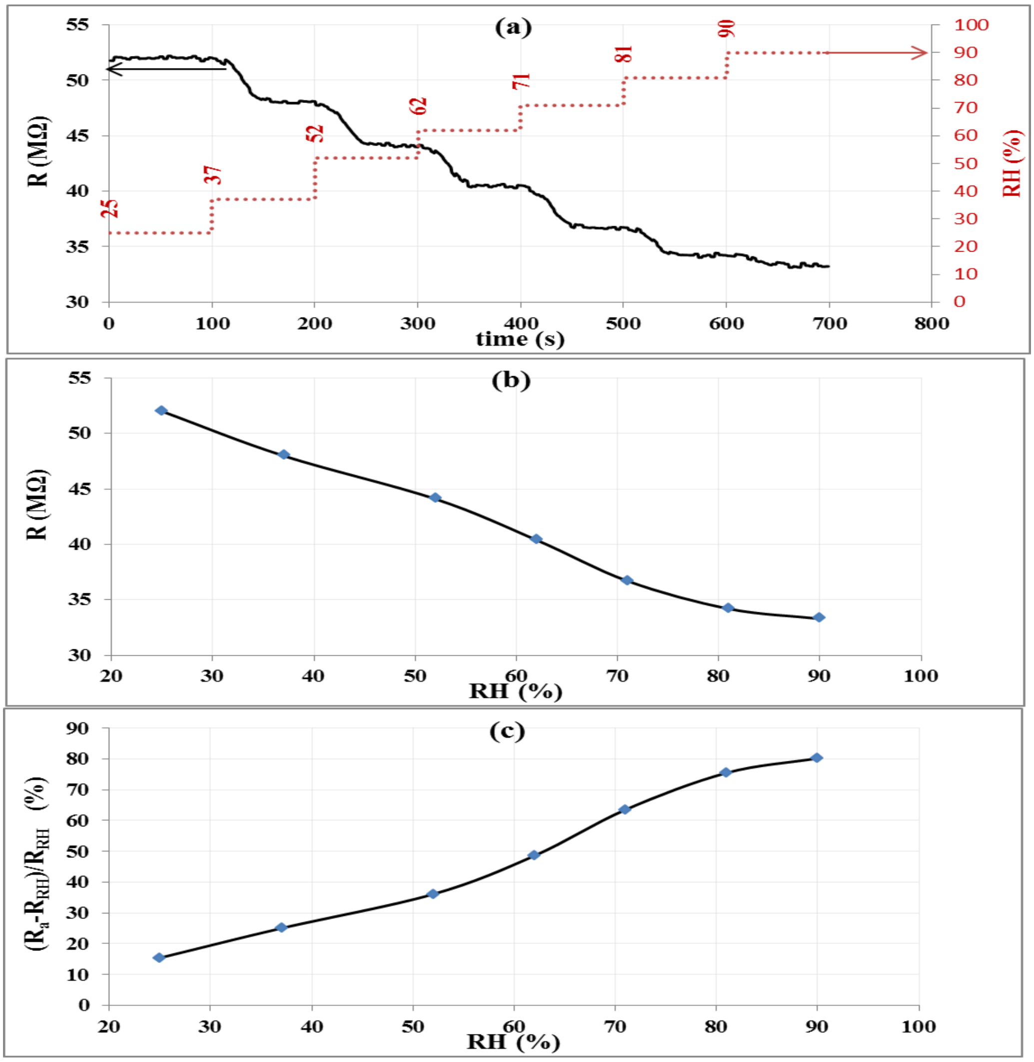

Figure 5-Variations in (a) resistance with time at different RH, (b) resistance with RH, and (c) sensitivity with RH, for the humidity sensor based on rf sputtered V_2O_5 (R_a is the resistance at the dry air; 10% RH).

In addition to the electronic conductivity, the increase in V_2O_5 conductivity with the increase in RH may be attributed to increasing ionic conductivity, which is highly dependent on the permittivity that is affected by absorbing humidity. The humidity significantly effect at low humidity levels. This may be due to the formation of layers of water molecules, which may accelerate the transport of ions according to the Grotthuss mechanism [17]. At lower relative humidity, the resistance drops rapidly, which may be attributed to some observable changes, such as the dissociation of particles that occur when moisture is absorbed [17].

Conclusions

The annealing temperature greatly influenced the structural and optical properties of the V_2O_5 thin films prepared by the rf sprttering. Thin films deposited on Si substrates and annealed at 500 ° C in air possess a highly orientation along the [001] direction with an increase in crystal size. FTIR spectroscopy also proved enhanced V2O5 bonds with annealing. The energy gap was also decreased with the increase in the annealing temperature, especially at 500 ° C, which in turn led to an increase in the conductivity of the samples. All these fundamental changes in the physical properties of the prepared film increase its efficiency as a humidity sensor. The samples demonstrated a marked change in conductivity for a wide range of relative humidity values, rendering them efficient to be used in fabricating humidity sensors.

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