Optical and Microstructure behavior on Vanadium doped (V-TiO_2) oxide films using magnetron reactive sputtering

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ABSTRACT

Vanadium doped Titanium dioxide (V-TiO_2) thin films were prepared using DC magnetron sputtering method. The samples were subjected to analysis of X-ray diffraction, SEM and optical studies. The XRD films revealed the crystallographic lattice planes such as (101), (200) etc. We report two observations, one was variation of partial O_2 pressure inside the chamber and other was temperature dependent. The broad peaks were assigned to $2\theta=25.313^{o}$ for (101) plane, $2\theta=37.684^{o}$ for (112) plane and $2\theta=48.084^{o}$ for (200) plane and intensity of interfacial planer planes was magnified with the temperature. SEM Micrographs show that tracks of annealed metal TiO_2 films were developed significantly and film phases were distributed uniformly with the temperature variation. EDAX reviled that the mean ratio of Ti:V was 52.35:47.65 and an evaluated Ti/V ratio was 1.10. The average size of the crystallite was also determined using Scherer formula and the structural parameters were determined on the basis of temperature dependent and the present work indicates the percent of transmission for electronic applications.

Key words: DC Magnetron sputter, TiO_2 thin films, XRD, SEM, Electrical parameters.

INTRODUCTION

Since 1980, a reactive sputtering of thin films is intensively investigated because the sputtering of metallic targets in the presence of reactive gas (RG) makes it possible to easily form compound films, such as nitrides, oxides, carbides or their combinations. The reactive sputtering process can be, according to the amount of RG used in the film deposition, divided into three modes: (a) metallic, (b) transition and (c) reactive [1-3]. A typical characteristic of the reactive magnetron sputtering is a low deposition rate of compounds produced in the reactive mode compared to that of the pure metallic or alloyed films produced in the metallic mode. The electrical conductivity of the sputtered target after its reaction is also important [4]. When the reaction product is electrically insulated, two further problems occur: (1) non-sputtered surfaces of the target are covered by thick dielectric layers, which are charged up, and cause an arcing when the charge achieves a threshold value; and (2) the anode of the magnetron disappears also due to its dielectric layer cover. The pure TiO_2 absorbs light with wavelengths shorter than 380nm (UV region), therefore it is a great challenge to increase its spectral sensitivity to visible light for more practical applications [5-6]. Vanadium doped TiO_2 (V-TiO_2) films are usually prepared by reactive deposition results in TiO_2 supported systems. Several experiments have shown that at temperatures higher than 600 K deposited vanadium diffuses quickly into the bulk of the substrate, leaving no vanadium at the surface. In order to produce a V-Ti mixed oxide that can endure high temperature annealing, TiO2 thin films with a thickness in the range of several nanometers as a host oxide are a way out provided that the vanadium can be stabilized in the layer. Titanium dioxide has been widely used in many applications in optical and technological fields [8, 9] and as a result of its innumerable advantages, among which its low cost and structural stability and it also stood out among the various semiconductor materials.

Thus, in the present paper, a full investigation of vanadium doped TiO_2 catalysts is presented. The thin films V-TiO_2 oxides were prepared and studied the characteristic behavior with the variation of partial oxygen pressure in the chamber. Also, the temperature effect on coated films understands with structural behavior [9-10]. We also reported an emission behavior of TiO_2 films at different temperatures. The transmittance effect on the fabricated TiO_2 thin films were described in detail with both variation of temperature and partial O_2 pressure. The behavior of electrical properties for both annealed and without annealed TiO_2 films were highlighted in the present paper. The prepared thin films were characterized by four probe method for electrical properties, XRD and SEM for structural behavior and U-V method for band gap energy. A lattice mismatch can be avoided in crystal with (110) surface is also employed as substrate for the growth of V-Ti mixed oxide layers.

PREPARATION AND CHARACTERIZATION TECHNIQUES

V-TiO2 thin films were deposited on a glass substrate by the magnetic reactive method in the laboratory. The cathode is a 50.6 mm diameter and 6 mm thick Ti plate with purity 99.95% used as such supplied from SISCO India Ltd. The base pressure prior to film deposition was kept below $4.0X10^{-4}$ pa and the discharge gas is Air with purity 99.99&. All the V-TiO_2 layers are deposited on borosilicate glass substrate (75mm X 25mm X 1.35mm) obtained from Polar Industrial Corporation, India. Both wafers and borosilicate glass substrate were cleaned sequentially in an ultrasonic bath using ethanol, acetone, and de-ionized water before they were

mounted on the sample holder. The samples were prepared at different substrate base temperatures. The variation of the temperature, time of deposition and influence of O_2 pressure in the chamber is noted in the Table 1. Composite films were deposited in a vacuum chamber. The vanadium, V vapor of diameter 50.6 mm and thickness 4 mm was used as solid source down to the cathode substrate. The real ratio of V/Ti was changed from 0.00 to 0.45. The air discharge pressure was kept $100X10^{-2}$ pa for all deposition of the thin films. The typical deposition parameters of the present study are given in Table 2.

Table 1: The Sputtered Parameters of TiO_2 films.

Parameter	Function
Power system	DC voltage: -2000 V and current 3 Amps)
Metal Target	Titanium purity: 99.995% Diameter: 50.8mm; thick: 4 mm Vanadium purity: 99.6% Diameter: 50.8mm; thick: 4 mm
Substrate	Glass (75 mm x 25 mm x 1.35 mm)
Distance of Substrate (T_S)	8.0 cm
Base pressure (Torr)	$4.5x10^{-6}$
O_2 Partial Pressure (Pa)	$0.5X10^{-2}$
Substrate Temperature	373 – 523 K
Sputtering Pressure (SCCM)	25
Power (Watt)	40 - 80 W
Cathode current	100 – 300 nA
Cathode potential	300– 400 V
Air flow rate (SCCM)	10

Table 2: V-TiO_2 thin films preparation parameters.

S. No	Physical parameter	Variation step
1.	Substrate temperature (º C)	300, 350, 400, 450, 500
2.	Deposition time (seconds)	200, 400, 600, 800
3.	Partial O_2 pressure (X10-4 Pa)	1.0, 1.4, 1.8, 2.0, 2.5

At first the chamber, a diffusion pump backed by a rotary pump with a liquid organ gas, was evacuated to an ultimate vacuum of $2X10^{-6}$ mbar. The pre-sputtering was done for about 30 minutes, before each deposition, both titanium and vanadium targets in pure argon to remove surface oxide layer formed if any on the target surface during exposure to air. Pure oxygen gas was admitted into the chamber through the needle valve and the required oxygen

partial pressure was set and allowed to stabilize. Argon gas was then introduced and the required sputtering pressure was maintained. The sputtering power in the range 40 – 80 W/cm^2 and substrate bias voltage in the range from 0 to -150 V were maintained in order to study the physical properties. In the present study, the chemical structure and planes of elements present were discussed using X-ray spectrometer and the percent of elements as well as grain size dependence have studied by using SEM analysis. The systematic electrical properties are discussed in detail using four-probe method with variable temperature.

RESULTS AND DISCUSSION

The cleaned titanium and vanadium targets were pre-sputtered for 5 mib in order to ascertain the same state of the targets in every run. Suitable powers were applied to each target to give similar deposition rates of V and Ti. The substrate holder was rotated axially at 2 rpm to achieve a uniform film composition. Both guns were tiled at an angle of 45º so that the plasma from both the targets can be concentric. The films deposited at room temperature were usually amorphous in nature. The films were deposited at high substrate temperature used as such for crystallization [12]. The plasma discharge was operated at a constant target power of 40 W at a down pressure of 1.0 X 10^{-4} Pa on grounded static substrates. The glow discharge behavior of V-Ti target provides the exact oxygen etch on the oxide layer to prepare V-TiO_2 films. The cathode voltage is changed between 400 to 500 V and oxygen pressure is varied from 1X10^{-5} to 2.4X10^{-3} mbar. When oxygen pressure is varying the cathode voltage was increased up to 1.2 mbar and then decreased and found that the operating O_2 pressure was 1.2 mbar at the target power of 60 W.

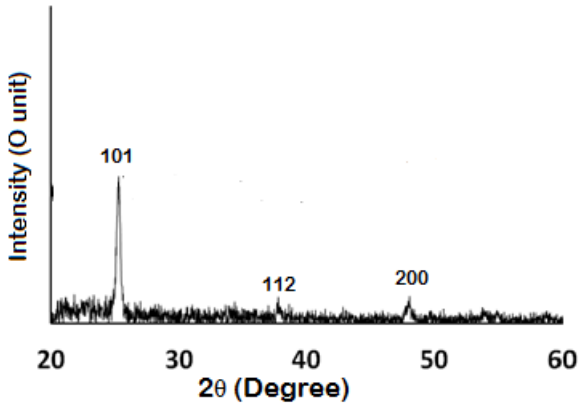

Fig. 1: XRD pattern of TiO_2 at 100º C.

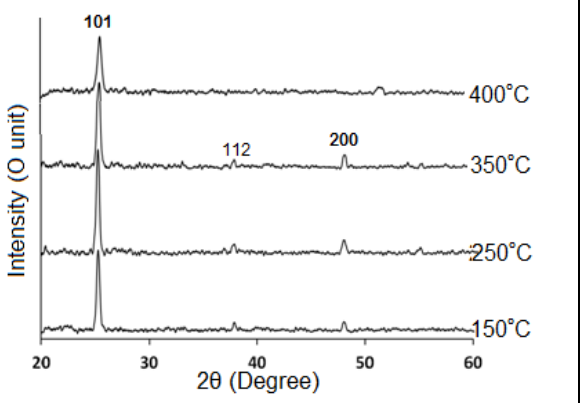

Fig. 2: XRD pattern of V-TiO_2 thin films.

XRD diffractograms in Fig. 1 and Fig. 2 that show relatively broad peaks at 2θ=25.313º ; 37.684º ; 48.084º were recorded from film deposited on TiO_2 and V-TiO_2 substrates at the annealed temperature, 100º C, 150º C, 250º C, 350º C and 400º C respectively. The broad peaks were assigned to 2θ=25.313º for (101) plane, 2θ=37.684º for (112) plane and 2θ=48.084º for (200) plane. The intensity was magnified with the temperature and interfacial planer planes were steady and not showing any displacements. Thus, vanadium deposition on Ti substrate does not affect the crystal structure and V-TiO_2 was also same structure of tetragonal with the lattice planes, a=4.59º A and b=2.95º A with cation radius of 0.75º A. In order to reveal the origin of the

increased reducibility of TiO_2 films by vanadium doping, examination of the oxidation states of vanadium and titanium in the mixed oxides was conducted. Fig. 3 shows the partial O_2 effect on the fabricated V-TiO2 thin films was also carried out at the film deposited temperature 250º C.

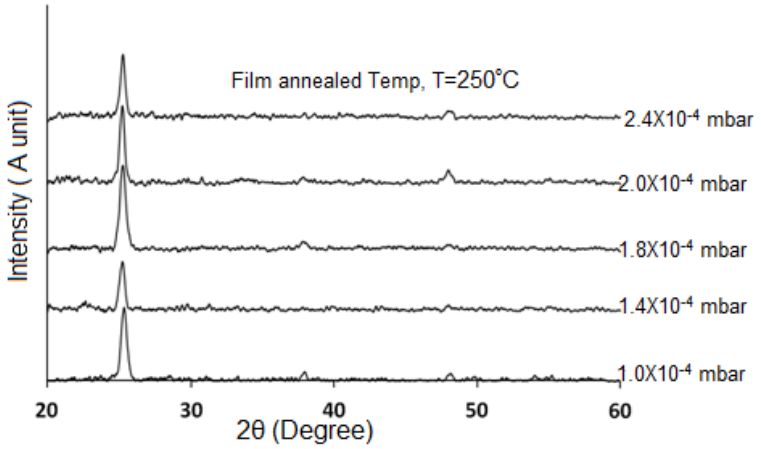

Fig. 3: Partial O_2 effect on V-TiO_2 films of XRD spectrum at 250º C.

There were no changes of TiO_2 lattice plane, (101) with O_2 pressure. However, the other crystal lattices were not developed significantly at the temperature, 250º C.

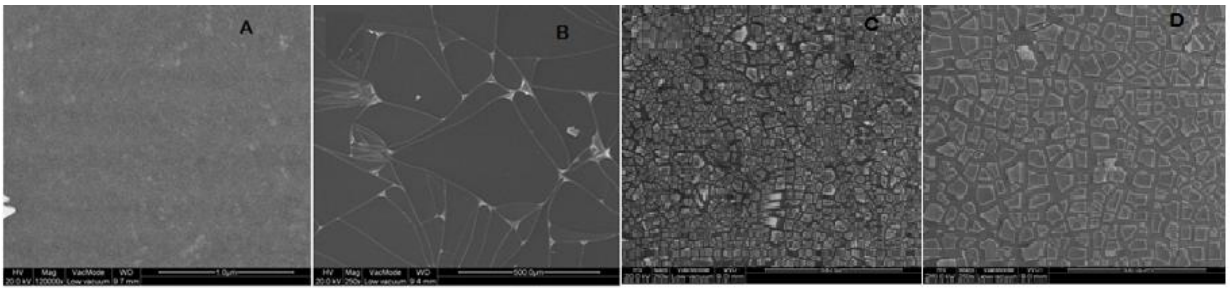

Fig. 5: SEM micrographs of V-TiO_2 films at (A): 100ºC; (B): 150ºC; (C): 250ºC; (D): 350ºC.

Fig. 5 shows the surface morphology of the TiO_2 films deposited at different temperatures and a constant O_2 pressure, 1.8 $X10^{-4}$ Pa. Micrographs show that tracks of annealed TiO_2 films were developed significantly. This indicates that the tracks were modified when increases the temperature and film phases are distributed uniformly. At high temperature, an enhanced tracks in the films were observed and this was due to the enhancing the oxygen partial pressures. The EDAX spectra taken for all the samples revealed a change in the composition of Ti and V in V-TiO_2 films. It was observed that argon and silicon were not found along with Ti and V elements and that was absent in other layers formed at high reacting temperatures. The elemental composition results obtained using EDAX analysis for V-TiO_2 thin films deposited at different temperatures were determined. All the films deposited at various temperatures show a similar spectrum confirming the fact that only Ti and V are present in the films. The mean ratio of Ti:V was 52.35:47.65 and an evaluated Ti/V ratio was 1.10. Thus, several phases of titanium were

observed in all ranges of temperatures and an elemental composition near to stoichiometry value which was also supported by XRD results studied for this investigation.

The electrical transport properties of the polycrystalline thin films strongly depend on their structure [14]. The electrical conduction mechanism depends on temperature in respective of their structure of the thin films. The variation of conductivity (σ) with the temperature is according to the thermal conduction mechanism relation

$$\sigma = \sigma_o \exp(-\frac{\Delta E}{kT}) \quad (1)$$

where ΔE represent the thermal activation energy of electrical conduction. σ_o is the conductance of semiconductor material and k is Boltzmann's constant.

Table 3: The variations of electrical properties of TiO2 thin films.

Substrate temperature (℃)	Electrical conductivity, σ, (Ω^{-1} cm^{-1})	Thermoelectric power, S (μVK^{-1})	Carrier concentration, n (cm^{-3})	Activation energy, ΔE, (eV)
100	$58.73X10^{-3}$	62.55	$6.27X10^{15}$	72.25
150	$56.42X10^{-3}$	66.25	$7.56X10^{15}$	68.22
250	$56.11X10^{-3}$	63.54	$8.37X10^{15}$	67.86
350	$56.25X10^{-3}$	61.23	$8.92X10^{15}$	65.25
400	$56.88X10^{-3}$	63.58	$9.08X10^{15}$	64.56

The conductivity of thin films depends upon the temperature of the substrate is shown in Fig. 6. All the films, the conductivity has a linear function of the temperature, decreases with the increase of substrate temperature. At every temperature the linearity of the line is observed. The activation energy is determined from the slop of lnσ versus 1000/T (K^{-1}) plot in the higher temperature range. It is observe that the activation energy decreases with the increase of the substrate temperature and values are noted the Table 3. The decrease of ΔE is estimated with the increase of substrate temperature. The thermoelectric power measurements were determined with the formula given below.

$$s = \frac{\Delta v}{\Delta T} \mu V / K \quad (2)$$

Where ΔT is temperature gradient and Δv is thermo e.m.f at absolute temperature. The thermoelectric power is also decreases with the increase the temperature. Thus, the variations of all electrical parameters are temperature dependent and negative sign of thermoelectric power suggest that conduction should occur due to free electrons. The drop of thermoelectric power with increase of temperature indicates that the electrons are exited into conduction band, which provide transport mechanism. The positive sign indicate that the fabricated thin films are p-type semiconductor and holes are contributing the transport behavior. The active energy was also temperature dependent and more than half of the TiO_2 polycrystalline actual energy 3.54 eV. The value obtained in this process is very large than *K*T value and describe the deep level state in the forbidden state.

CONCLUSION

Vanadium doped TiO_2 metal oxide thin films were prepared using DC magnetron reactive method. The temperature effects on electrical and structural properties were observed. The significance structural development of thin film was detected at substrate ambient temperature, 350º C. The thin films deposited at various temperatures show a similar spectrum confirming the fact that only Ti and V are present in the films with the ratio of Ti:V was 52.35:47.65 and an evaluated Ti/V ratio was 1.10. The founded activation energy is more the half of its polycrystalline value and good agreement with theoretical one. The origin of the increased reducibility of TiO_2 films by vanadium doping, examination of the oxidation states of vanadium and titanium in the mixed oxides was conducted.

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