IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 11, Issue 4 Ser. II (Jul. – Aug. 2019), PP 60-70
www.iosrjournals.org

Morphological and Humidity Sensing Studies of Pure WO_3

N.K. Pandey and Sanchita Singh
(Sensors and Materials Research Laboratory,
Department of Physics, University of Lucknow,
Lucknow, 226007, U.P., India)

Abstract: Present paper deals with a sensing performance of pure WO_3 at different annealing temperatures, the sensing properties and characterization of pure WO_3. Pure WO_3 have been prepared through solid state reaction route. These samples have been annealed at temperature (300°c-600°c) for three hours and then exposed to humidity chamber. At 600°c temperature we find out the highest sensitivity of WO_3 which is 10.40 MΩ⁄RH%. As calculated from Scherer's formula crystallite size for the sensing elements of pure WO_3 is 72.4 nm. Structural properties studied by X-Ray diffraction method. SEM micrograph reveal that as the temperature increases the porosity of materials increases forming clusters for WO_3. This feature shows the adsorption and condensation of waters vapours. Now the grain size of pure WO_3 at annealing temperatures 300°c, 400°c, 500°c and 600°c are 114nm, 135nm, 148nm and 158 nm respectively. The pressed powder pellets have been annealed in air at temp.300°c to 600°c for 3hours and checked for its sensing efficiency. Each heat treated pellet was exposed to humidity under controlled condition and variations in resistance with the humidity were recorded.
Keywords: Sensitivity, Humidity, Nanostructures, Resistance and Surface Morphology.

Date of Submission: 15-08-2019 Date of Acceptance: 30-08-2019

I. Introduction

Sensors are key elements in the rapidly evolving fields of measurements, instrumentations and automated systems. In this paper we prepare the humidity sensor by materials. Humidity is a permanent environmental factor. Humidity is the amount of water vapour in the air. In this paper we prepare the metal oxide ceramic humidity sensor. Metal oxide ceramic humidity sensors based on porous and sintered. Oxides have attracted much attention due to their chemical and physical stability. Research has been going onto find suitable materials that show good sensitivity over large range of relative humidity (RH), low hysteresis and properties that are stable. Among the metallic oxide, tungsten oxide (WO_3) has many technological applications. It is good electrochromic, optochromic and gasochromic material. WO_3 behave like n-type semiconductor. WO_3 is an important kind of wide bandgap, semiconducting metal oxides. Aihua yan et al. have synthesized WO_3 nanowall using solvothermal(1). Su et al. prepared WO_3 thick film using screen printing method(2). Z hou et al. highly ordered mesoporous tungsten oxide have been synthesized via the hard templating method(3). Liu et al. have synthesized tungsten oxide nanorods assembled microspheres by a facile hydrothermal process(4). Metal oxide semiconductor (WO_3) have attracted significant attention towards gas sensing and humidity sensing due to their simple implementation, low cost and good reliability for real time control system with respect to other sensors. In ceramic oxide water molecules are adsorbed to increase the conductivity of n-type ceramics and to decrease the conductivity of p-type ceramics, because the conductivity is related to the no of free electrons of surface .This type of sensing is called "electronic type"

Now we trace the sensitivity of semiconductor. We have reported characterization and humidity sensing studies of (pure) WO_3 prepared by solid state reaction route and also show the characterization for WO_3 at 600°c annealing temp. by XRD and SEM.

Preparation of sample and experimental details

first of all we prepare samples of pure WO_3 by solid state reaction route .The materials WO_3 (Loba Chemie, 99.99%). Now take a wo_3, 5wt%polyvinyle alcohol (pva) has been added as a binder because it increases the strength of materials. The powder have been mixed uniformaly and made fine by grinding in mortar with pastle for 3hours. The resultant powder have been pressed into pellet shape by uniaxially applying pressure of 250 Mpa in a hydraulic press machine (M.B. Instruments, Delhi, India) at room temp. The pellet samples prepared are in disc shape having diameter of 12 mm and thickness 2mm. The pressed powder pellets have been annealed in air at temp.300°c to 600°c for 3h in an electric muffle furnace (Ambassadar,India). After sintering, samples have been exposed to humidity in a specially designed humidity control chamber. Inside the humidity chamber,

a thermometer (+_1°c) and standard hygrometer (digital ,+_1%RH)are placed for the purpose of calibration. Variation in a resistance has been recorded with change in% RH. When resistance gets increases then relative humidity decreases at different temperatures. Variation in resistance of the pellet has been recorded by a multifunctional digital multimeter (±0.001 MΩ.VC-). Copper electrode has been used to measure the resistance of the pellet. The resistance of the pellet has been measured normal to the cylindrical surface of the pellet. We use the K_2So_4 solution as a humidifier and KOH sol. as dehumidifier. To see the effect of ageing, the sensing properties of these elements have been examined again in the humidity control chamber after six months. In this paper pure wo_3 indicated by "W".This experimental work shown by fig(1).

Principle of operation of WO_3

The mechanism of interaction of water vapour molecules with a porous metal oxide. It is proposed that the water vapour chemisorbs on the surface of metal oxide to form hydroxyl groups. The hydroxyl group with an adjacent surface -2 ion. The adsorption of water molecules on the surface takes place via a dissociative chemisorptions process which may be described in a two step process a given below.

1-water molecules adsorbed on grain surface react with the lattice A (A→W) as

$$H_2O + O_0 + A \leftrightarrow 2OH - A + V_0 + 2e^-$$

Where O_0 represent the lattice oxygen and V_0 is the vacancy created at the oxygen site according to the reaction

$$O_0 \leftrightarrow O^{2-} + V_0$$

2-Doubly ionised oxygen , displaced from the lattice ,reacts with the H+ coming from the dissociation of water molecules to form a hydroxyl group as given below

$$H^+ + O^{2-} \leftrightarrow OH^-$$

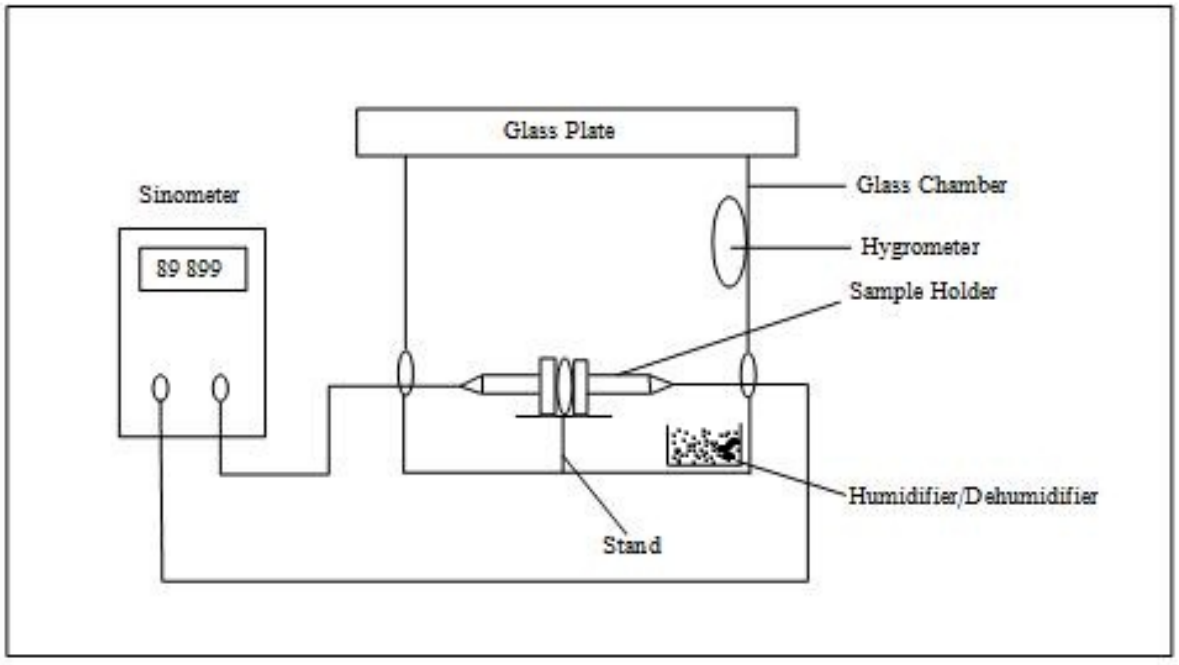

Fig.01: Systematic diagram of humidity sensing apparatus.

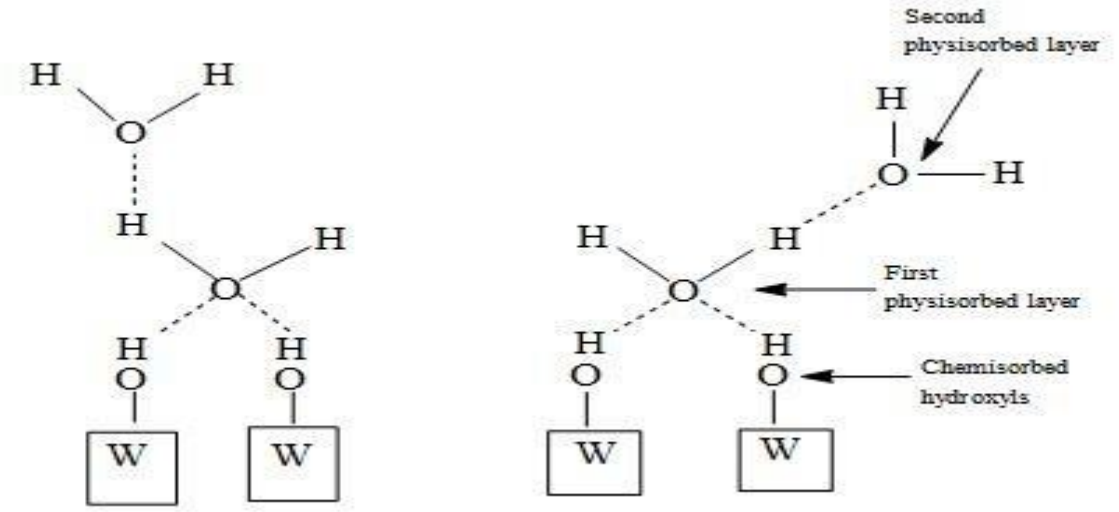

Fig.02; Sensing Mechanism of solid state humidity sensor

II. Result and discussion

Table 01: Sensitivity of pure wo_3

Annealing Temp. °C	a		b		C	
	10-50	50-99	10-50	50-99	10-50	50-99
300°C	14.8	1.79	15.14	1.32	13.32	1.57
400°C	17.72	1.59	17.87	1.32	15.87	1.12
500°C	14.36	2.95	18.75	2.00	19.77	2.00
600°C	17.42	4.67	18.25	4.06	14.97	3.89

a = Increasing cycle of relative humidity, b= Decreasing cycle of relative humidity, c = increasing cycle of relative humidity (after six months)

Table 02:

Sensitivity of sample (MΩ%RH) in the 10-99% RH range			
Annealing Temp. °C	a	b	c
300°C	7.64	7.52	6.85
400°C	8.84	8.76	7.75
500°C	9.53	9.52	9.98
600°C	10.4.	10.43	8.87

*1-**Humidification graph**:* In fig.(03) variation in resistance with the change in relative humidity has been recorded for the sensing elements of pure WO_3 at annealing temp.300°C-600°C. All the results have been found to be repeatable. There is continuous decrease in the value of resistance with increase in the %RH for the samples pure wo_3 at annealing temp 600°C are showing higher values of sensitivity. Fig(3) shows large decrease in the value of resistance for the initial value of relative humidity from 10%- 50%RH while in 50%-99%RHrange the fall in resistance is slow and for both range the sensitivity of W are17.42MΩ⁄%RH and 4.67MΩ⁄%RH-respectively. In the n-type semiconductor at high humidity condition(>50%RH)and low humidity condition (<50%RH).Because for the low humidity condition electrons may be trapped by the surface defect are released when the water molecules are co-adsorbed onto the surface causing the some of the oxygen ions to be desorbed and relatively high resistance at low humidity is maintained . At high humidity condition (>50%RH) the electrons may be trapped by the surface defects such as ionised oxygen vacancies and that these may be released when water molecules are adsorbed onto the defect sites and therefore resulting in reduce of the value of resistance at high humidity.

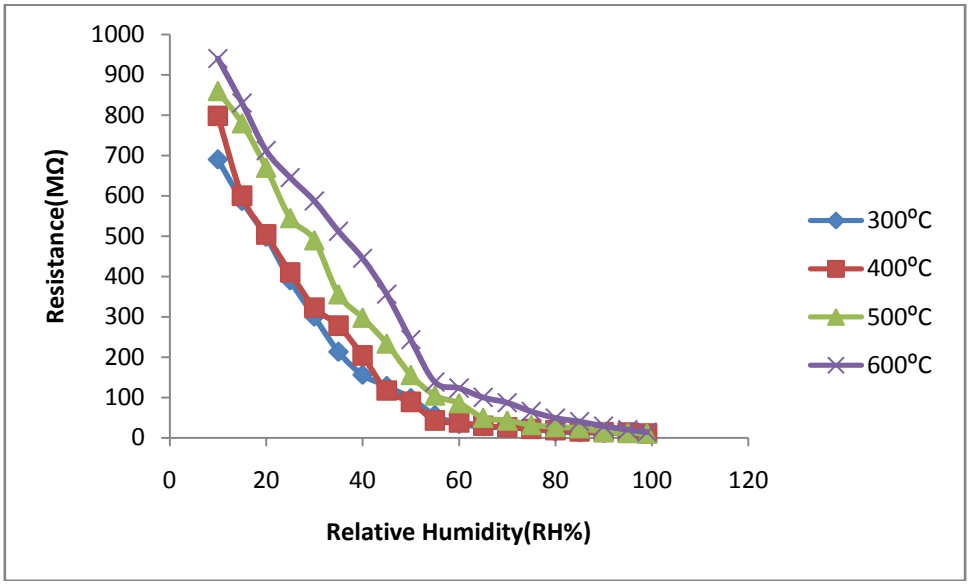

Fig.03: Variations in Resistance with % RH for Sample Pure WO_3 annealing temperature at 300°C to 600°C(Humidification graph)

*2-**Sensitivity comparison graph**:* Fig.(04) is the sensitivity graph for pure Wo_3(W) at (300°C-600°C) for the range 10% to 99%RH. The sensitivity of pure Wo_3 increases with increase of annealing temperature at 600°C. Pure Wo_3 shows highest value of sensitivity at 600°c .The average sensitivity for range 10% to 99%RH for pure Wo_3 is 10.40 MΩ/%RH at annealing temperature 600°C.Which is shown in table 2.The sensitivity of all samples at annealing temperatures 300 to 600°C increases when the temperatures gets increases.

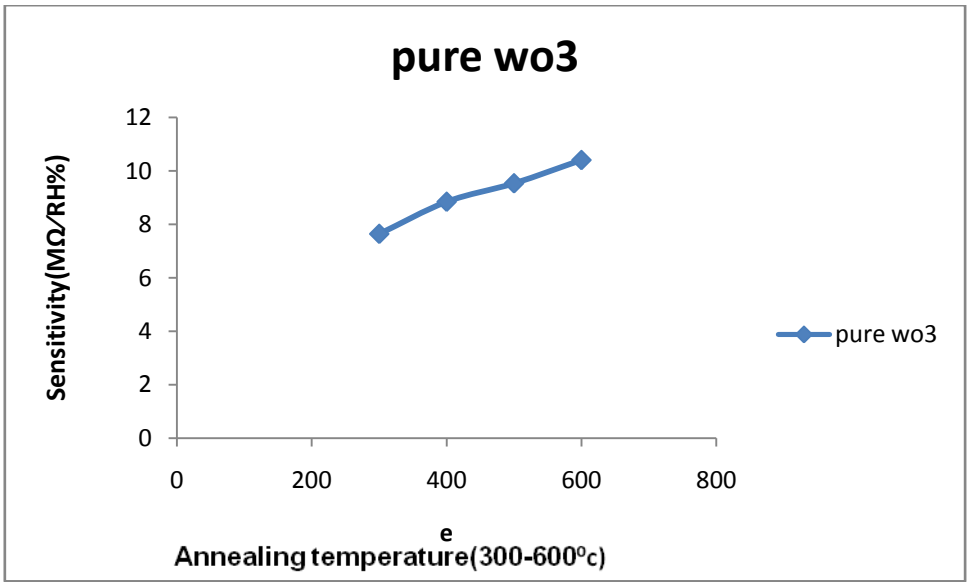

Fig.04: Sensitivity graph for Humidification cycle

***3-Hysteresis graph**:* Fig (5),(6),(7), and (8) shows the hysteresis graphs for Wo_3 at annealing temp.300 to 600°C.The phenomenon hysteresis may be understood in the manners that due to the adsorption of water on the surface of the sensing elements a chemisorbed layer form. Chemisorbed layer can be thermally desorbed only. Hence in the decreasing cycle of %RH, the initially adsorbed water is not removed fully leading to hysteresis. The value of hysteresis for sensing element W is .47% at annealing temperature 600°C which is less for highest temperature .

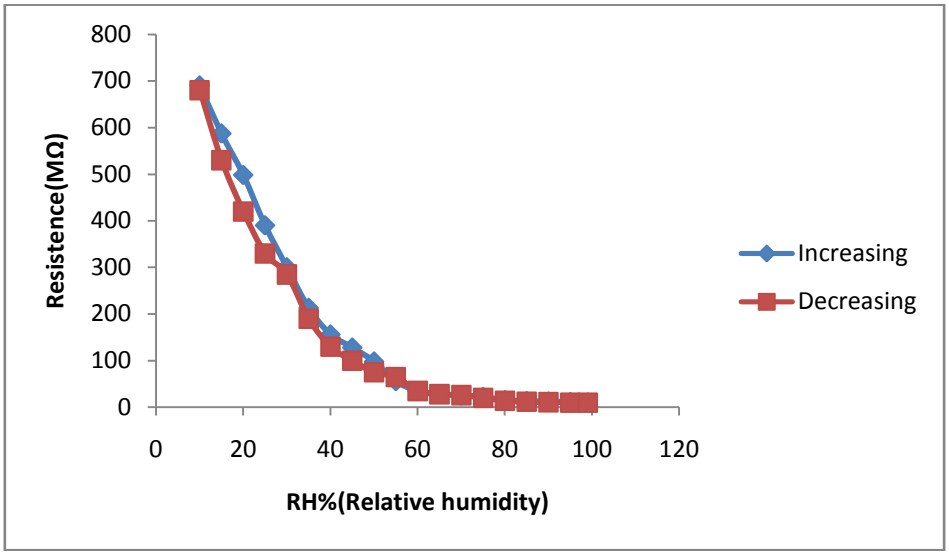

Fig. 05: Hysteresis graph for the sensing element Pure WO_3 annealed at 300°C

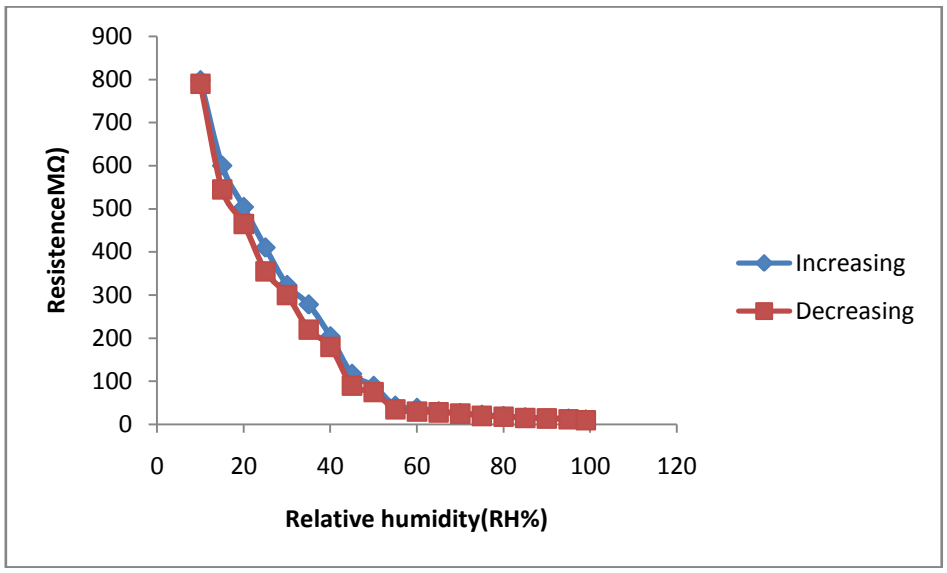

Fig. 06: Hysteresis graph for the sensing element Pure WO_3 annealed at 400°C

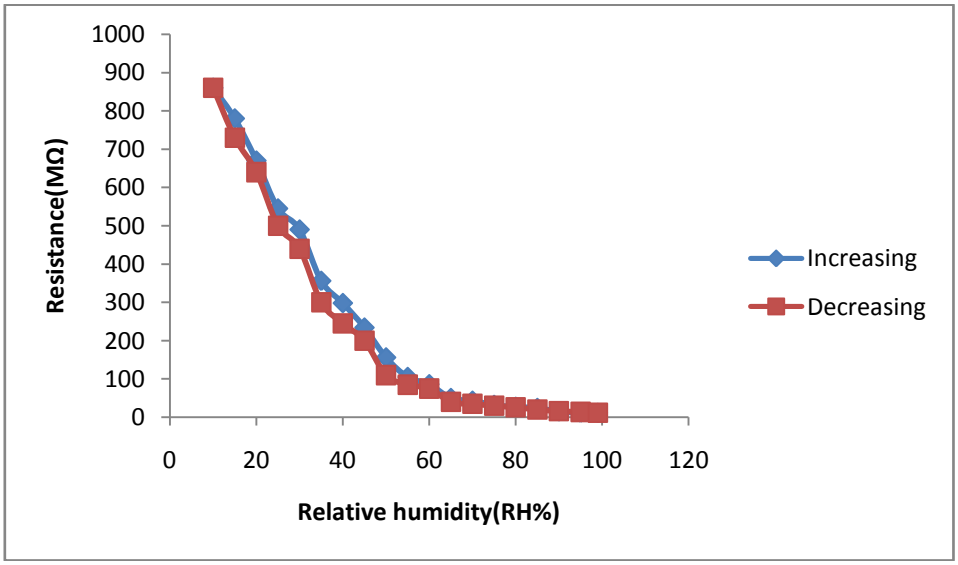

Fig. 07: Hysteresis graph for the sensing element Pure WO_3 annealed at 500°C

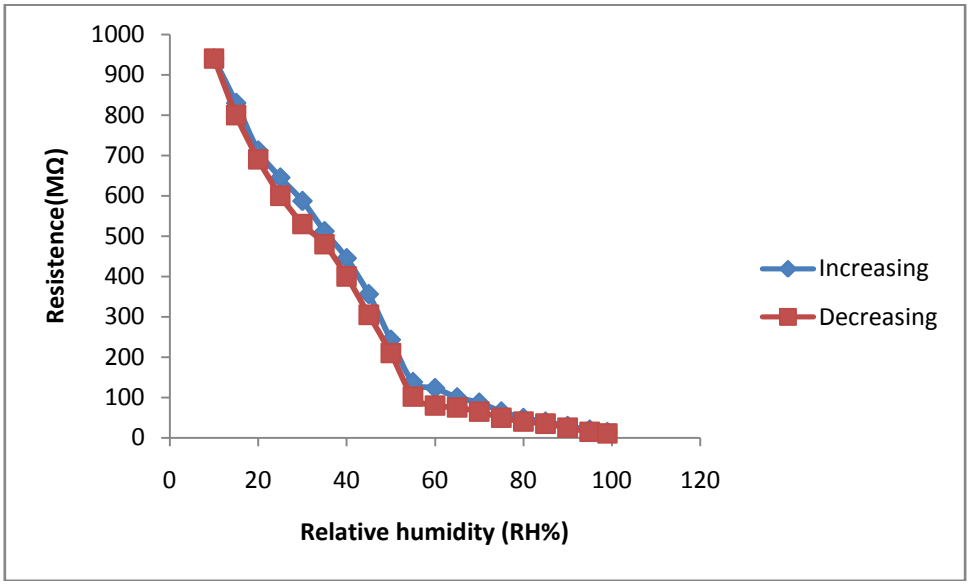

Fig. 08: Hysteresis graph for the sensing element Pure WO_3 annealed at 600°C

4-Ageing effect: The sensing properties of the samples W at annealing temp.300 to 600°C have been examined again in the humidity control chamber after six months and variation of resistance with %RH recorded. The variation of resistance of sensing elements WO_3 with change in %RH after six months have been shown in fig 09,10,11 and 12 for annealing temperatures 300°C,400°C,500°C and 600°C respectively. In this figures the value of average sensitivity in the range 10% to 99%RH of pure WO_3 at 600°C is 10.40MΩ%RH and after six months is 8.87MΩ%RHwhich are highest remaining to all temperatures, which is shown in table 2. Fig.(13) shows the combined ageing graphs and fig.(14) shows the sensitivity graph for ageing effect .Fig(15) shows the sensitivity comparison graphs for both humidification and ageing samples.

Result shows that the sensitivity less decrease with the time period and samples have less effect of ageing and low hysteresis.

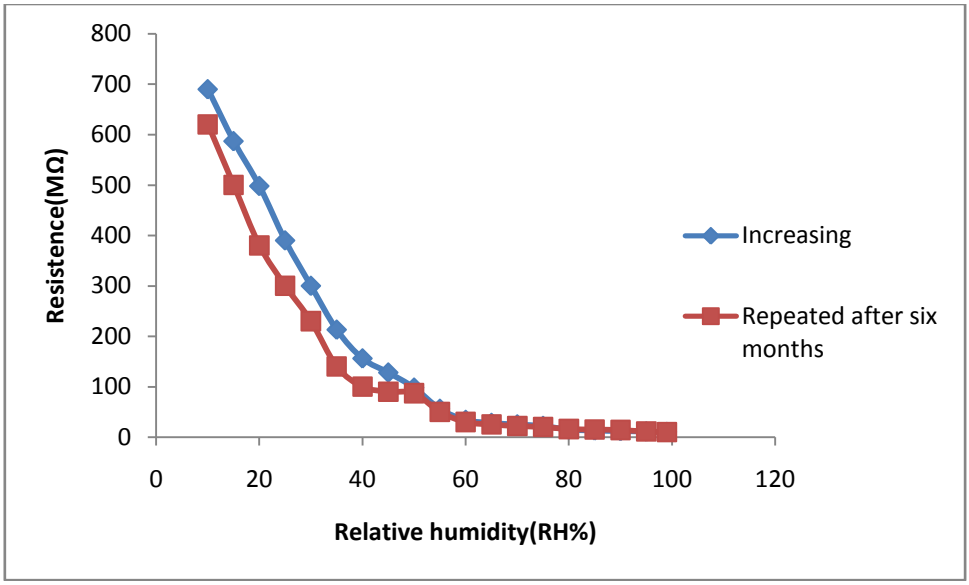

Fig. 09: Variations in Resistance with % RH for Sample Pure Wo_3annealed at 300°C (After Six months)

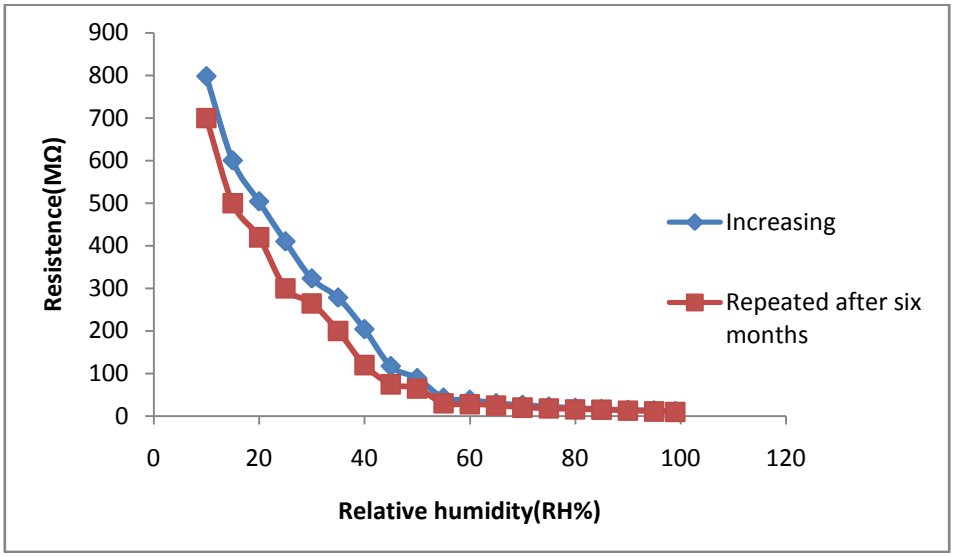

Fig. 10: Variations in Resistance with % RH for Sample Pure Wo_3annealed at 400°C (After Six months)

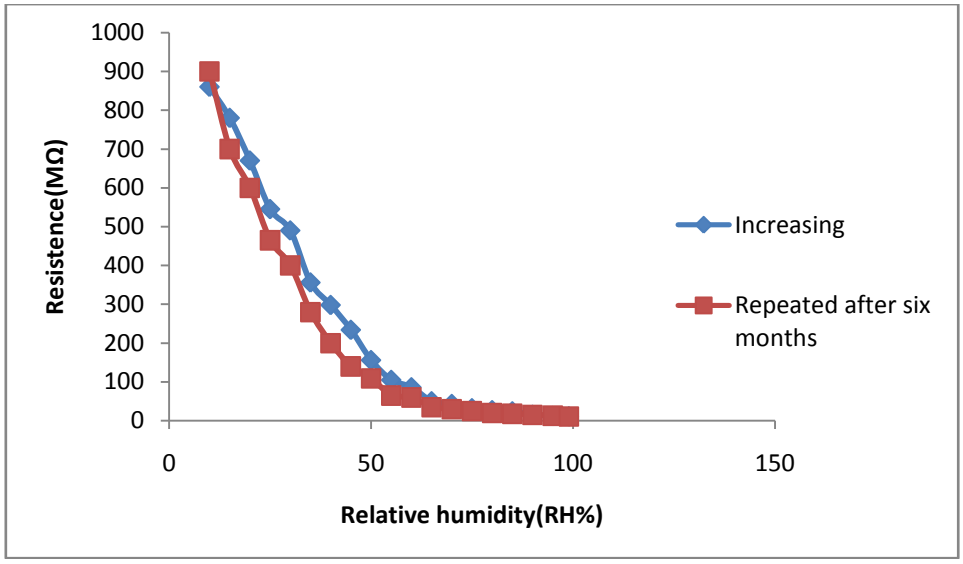

Fig. 11: Variations in Resistance with % RH for Sample Pure Wo_3annealed at 500°C (After Six months)

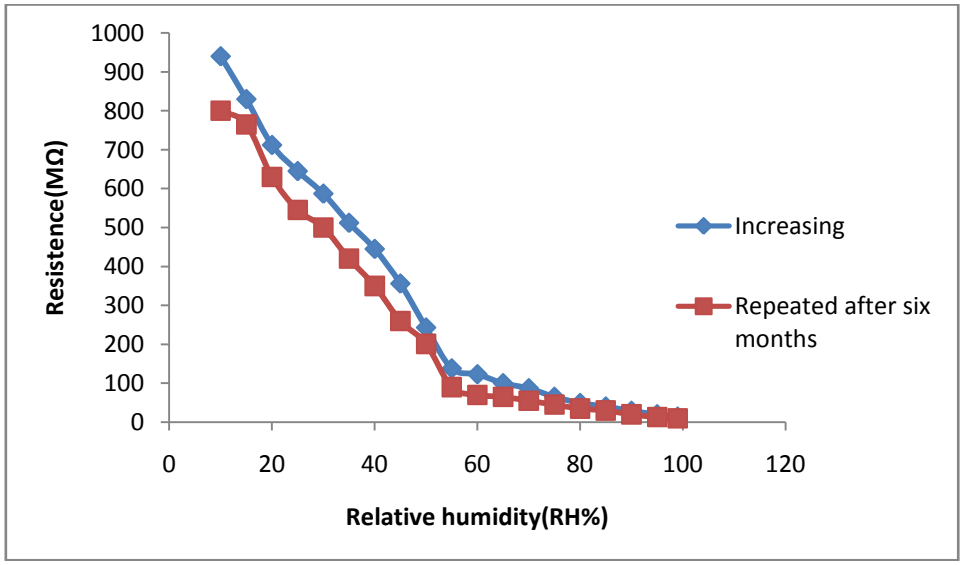

Fig. 12: Variations in Resistance with % RH for Sample Pure Wo_3annealed at 600°C (After Six months)

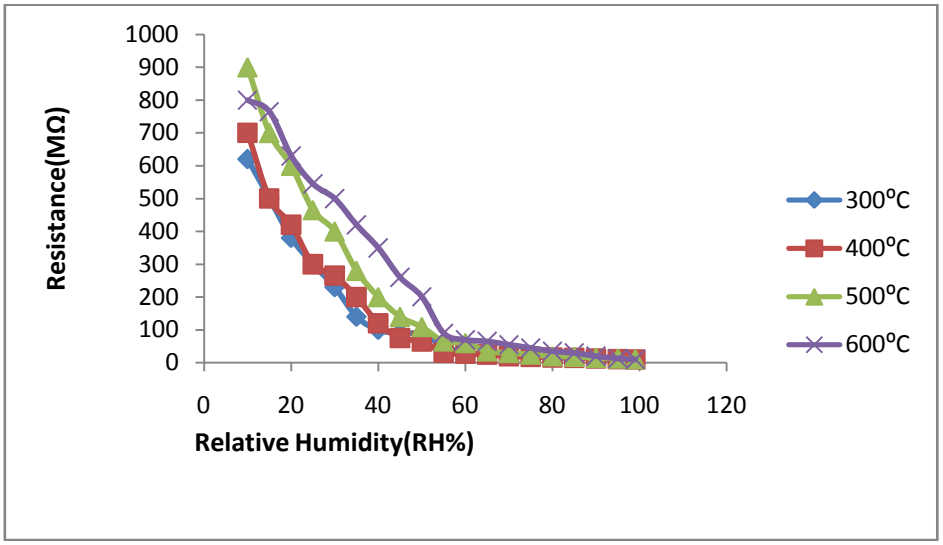

Fig.13: Variations in Resistance with % RH for Sample Pure WO_3 annealing temperature at 300°C to 600°C(Ageing Graph)

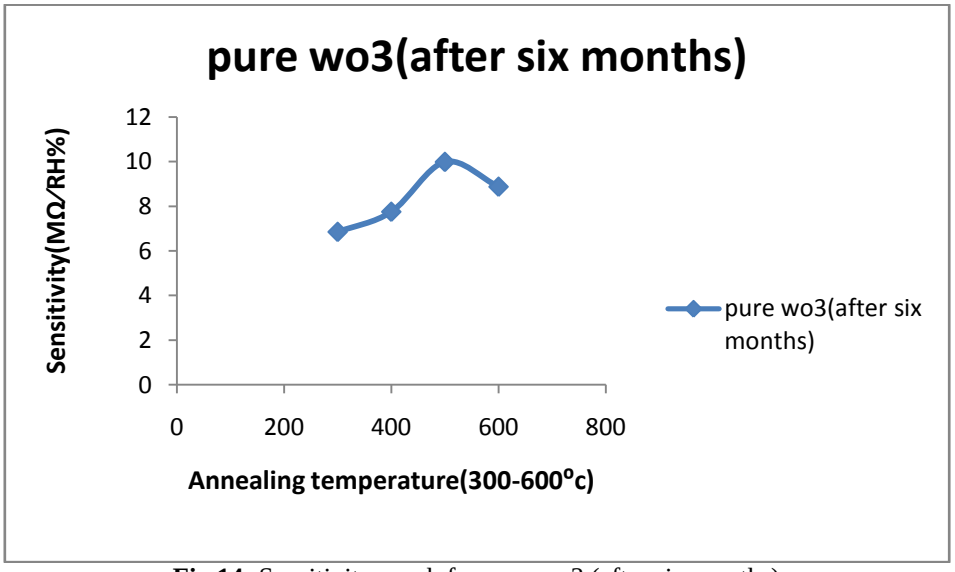

Fig.14: Sensitivity graph for pure wo3 (after six months)

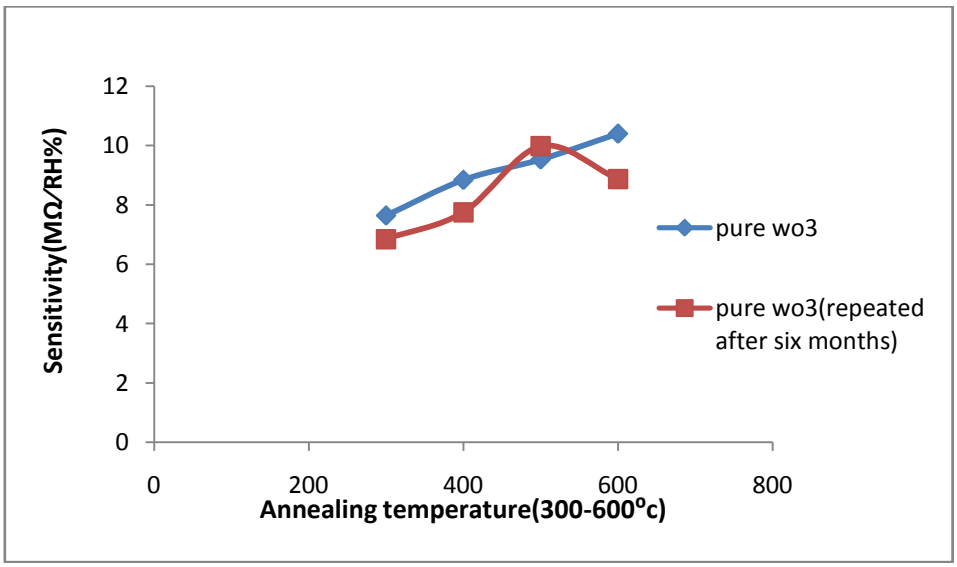

Fig.15: Sensitivity Comparison graph for humidification and Ageing cycle pure wo3 (after six months)

Characterization: (1)-scanning electron micrograph: Surface morphology of sensing element has been studies using scanning electron microscope unit (SEM, leo-0430, and Cambridge). The pure WO_3 sample at annealing temperature 600ºC have a best sensitivity ,low hysteresis, less effect of ageing and high reproducibility. FIG.(16),(17),(18),(19), shows scanning electron micrograph of pure WO_3 **at** annealing temperatures 300ºC,400ºC,500ºC and 600ºC ºC respectively. SEM shows that molecules of WO_3 particles form flakes and lots of pores. These pores are expected to provide sites for humidity adsorption. SEM reveals that the surface morphology is characterized by typical porous structure and small crystallites without inside pores but many inter grain pores. The grain size of pure WO_3 at annealing temperatures 300ºC, 400ºC, 500ºC and 600 ºC are 114nm, 135nm, 148nm and 158 nm respectively.

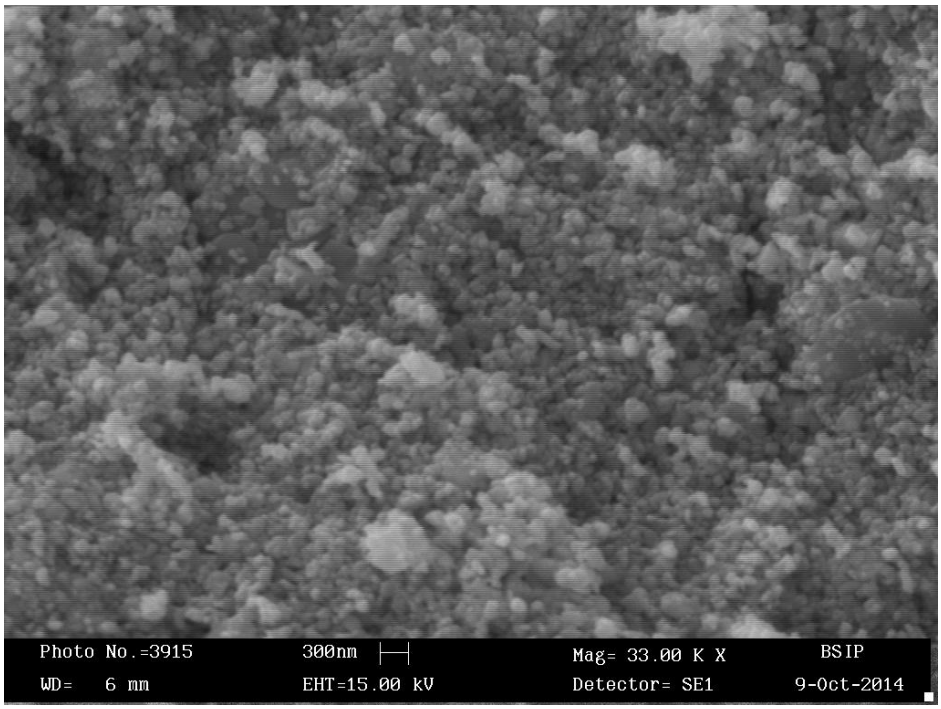

Fig. 16: SEM Micrograph of Sensing Element Pure Wo_3annealed at 300ºC

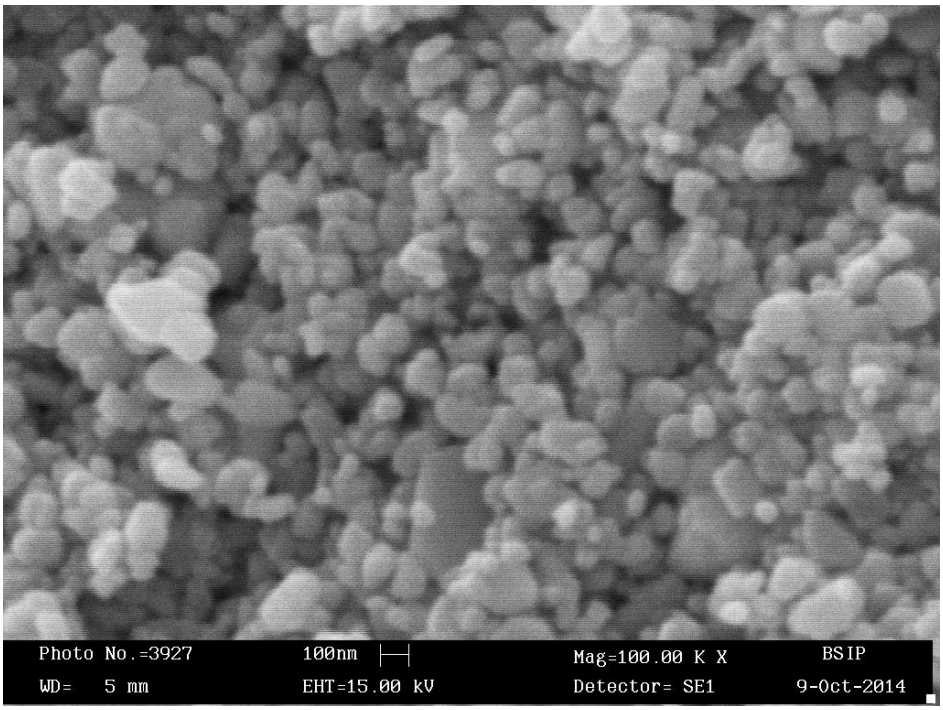

Fig. 17: SEM Micrograph of Sensing Element Pure Wo_3annealed at 400ºC

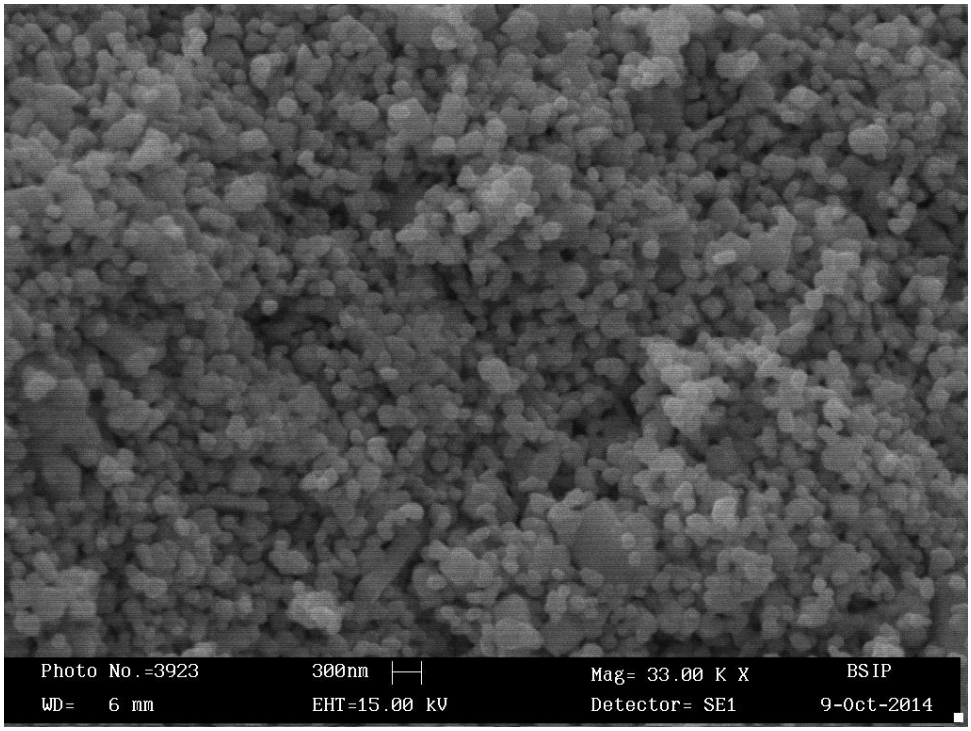

Fig. 18: SEM Micrograph of Sensing Element Pure Wo_3annealed at 500°C

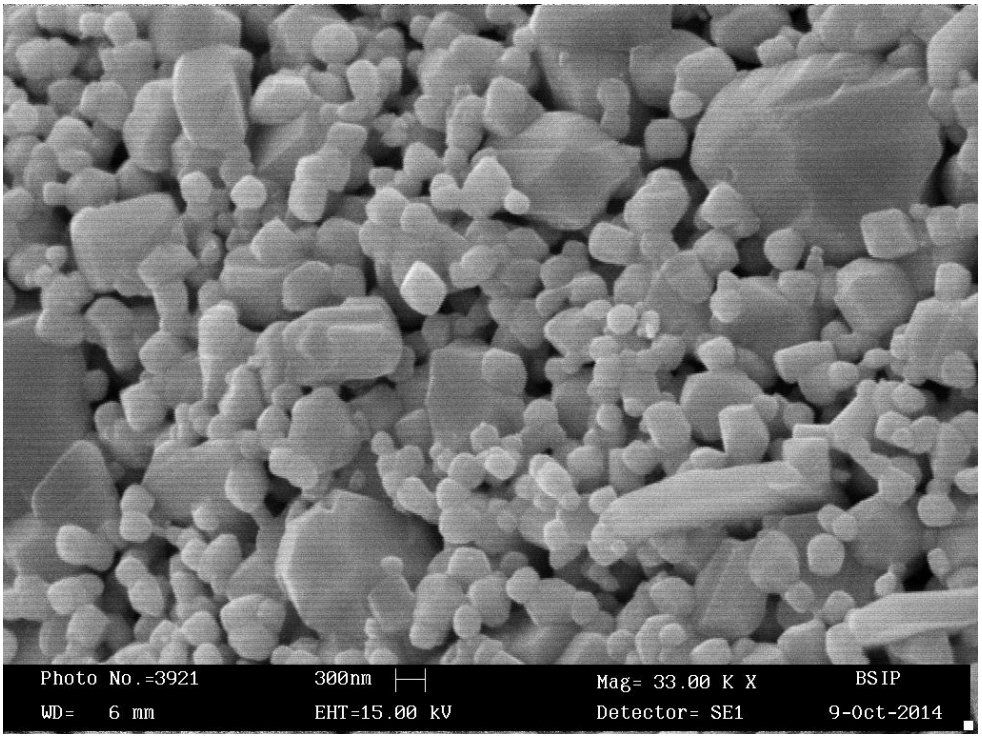

Fig. 19: SEM Micrograph of Sensing Element Pure Wo_3annealed at 600°C

(2)-X-Ray diffraction analysis: X-ray diffraction has been studies using XPERT PRO – Analytical XRD system (Netherland). The wavelength of the CuKα shows used 1.54060 A°. Fig.(20) shows X-ray pattern for the sensing elements (W) at annealing temp 600°C prepared at room temp. The average crystallite size of the samples has been calculated using Debye Scherer's formula D=Kʎ/β cosθ where D is the crystallite size , K is the fixed number of 0.9, ʎ is the X-ray wavelength ,θ is the bragg angle and β is the full width at half maximum of the peak , the crystallite size calculated from Scherer's formula for the sample **pure** WO_3 at annealing temp.600°C is found to be 72.4 nm.

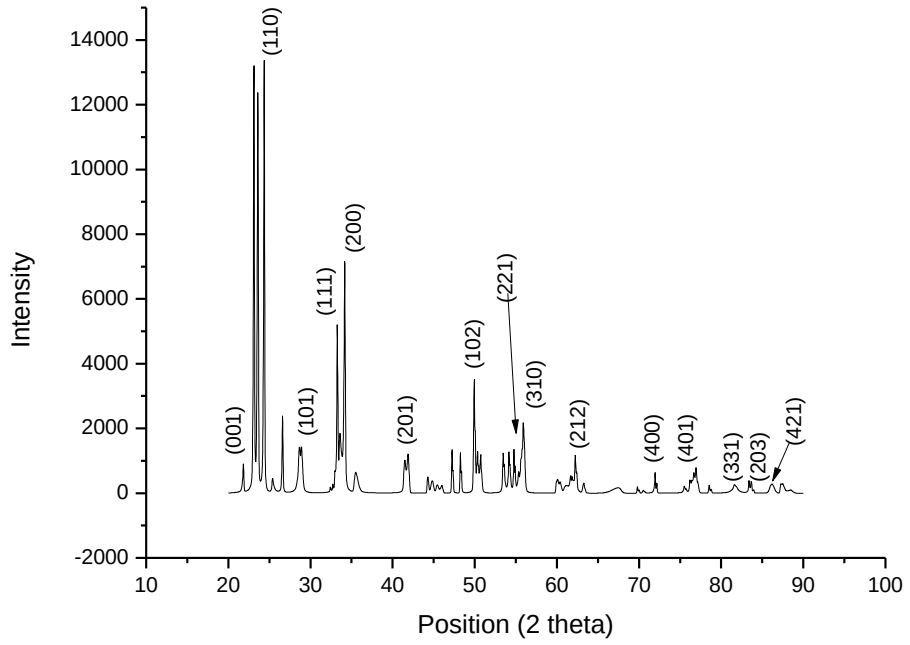

Fig.20: XRD pattern for sample pure Wo_3

III. Conclusion

The comparative studies of all samples of WO_3 shows that the average sensitivity of WO_3 at annealing temperature 600°C are 10.40MΩ%RH which is highest in comparison to all temperatures. . Now wo_3 shows best sensitivity, low hysteresis, less effect of ageing and higher reproducibility at annealing temp 600°c. The grain size of wo_3 at annealing temperature 600°C is 158 nm and crystallite size is 72.4 nm its shape is tetragonal.

Acknowledgements

The author would like to thanks The Birbal Sahni, Lucknow university, Lucknow and Physics department, Lucknow university, Lucknow, for providing SEM and XRD respectively.

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