Preparation and Characterization of Titania Thick Film Resistors

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ABSTRACT

Titania (TiO2) thick films prepared by standard screen printing technique and fired at different temperatures in air atmosphere. The compositional, morphological and structural properties of films were analyzed by Field Emission scanning electron microscopy (FESEM), Energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The films were observed to be oxygen deficient, it indicates that the films are non- stoichiometry in nature. As deposited and fired films were analyzed using SEM to know its surface morphology. XRD showed the polycrystalline nature having anatase and mix anatase-rutile structure. The crystallite size changes from 25.1695 nm to 62.3517nm for strong orientation (101) with increase in firing temperature.The role of firing temperature on electrical resistivity has been studiedand showed decrease in resistance with increase in temperature.

Keywords: Thick films, FESEM, XRD, Structural properties, Electrical properties.

INTRODUCTION:

Screen printing technique was introduced in the later part of 1950's to produce compact, robust and relatively inexpensive hybrid circuit for many purposes. Later on thick film technique has attracted by the sensor field [1]. Thick films are suitable for gas or humidity sensors since the gas sensing properties are related to the material surface and the gases are always adsorbed and react with the films surface [2]. Screen printing is simple and economical method to produce thick films of various materials [3-10]. The semiconducting metal oxides such as TiO2, SnO2, ZnO, Fe2O3, and WO3 etc. offer the potential for developing portable and inexpensive gas sensing devices, which have advantages of simplicity, high sensitivity and fast response. The sensor is a device senses input signal. The working principle of these semiconductor gas sensors is based on change in conductivity when exposed to the target gases [11]. TiO2 is a widely studied transition metal oxide and behaves as n-type semiconducting oxide due to non-stoichiometry. It has been widely studied for several applications in photoelectrical and optical fields and used as gas sensor. Several deposition methods have been used to grow TiO2 films such as Spray pyrolysis, Vacuum evaporation, chemical vapor deposition, magnetron sputtering, pulsed laser deposition, sol-gel technique, screen printing technique [12]. Titanium dioxide can be synthesized in three crystalline phases: rutile, brookite and anatase [13]. TiO2 in the anatase crystalline phase is one of the most studied materials for photo catalysis properties than rutile. Among the various metal oxides that can be used in gas sensors,

only those materials based on titanium oxide have been widely manufactured and utilized [14].

EXPERIMENTAL DETAILS:

Calcination, Drying and firing of Thick Film:

The glass substrates used for screen printing were cleaned initially by soap solution. Further, they were cleaned by using chronic acid to remove the finger prints and other impurities present on the substrates. Finally substrates were washed by distilled water and then clean with acetone.

Table 1: Preparation of TiO2 films.

1	Substrate material	Glass
2	Active Material	TiO2 (AR Grade)
3	Deposition Technique	Screen Printing
4	Types of screen	40S-Mesh No.355
5	Material Calcined time	1 hour.
6	Calcined temperature	4500c
7	Active Material to Organic vehicles ratio	70:30
8	Organic vehicles (Binders)	BCA & EC
9	Setteling time	15-20 minutes.
10	Drying under IR	45 minutes.
11	Firing Time	2 hours.
12	Peak firing temp.	3500C,4500C &5500C

Structural and morphological characterization:

The structural properties of TiO2 films were investigated using X-ray diffraction analysis from 20-800 withCuKα, λ=0.1542 nm radiation with a 0.10/step (2θ) at the rate of 2 s /step. FESEM was employed to characterize the surface morphology. The composition of TiO2 thick film samples were analyzed by an energy dispersive X ray spectrometer

The crystallite size was determined using Scherer's formula [15].

$$D = 0.9\lambda / \beta \cos\theta \quad \text{---------- (1)}$$

Electrical characterization:

The DC resistance of the film samples was measured in home-built static measurement system by using half bridge method as a function of temperature[16].

The electrical resistivity (ρ) of thick film resistor was determined by using the equation,

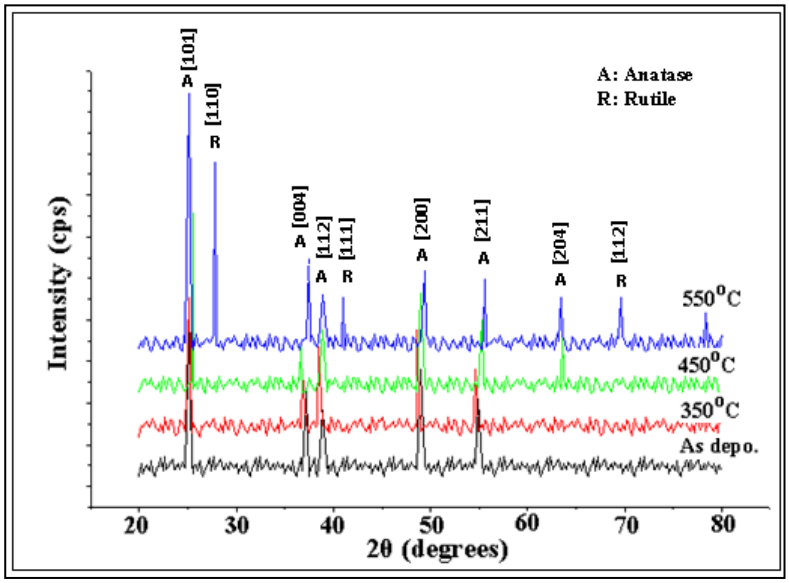
$$\rho = (R \times A) / l \quad \text{---------- (2)}$$

RESULTS AND DISCUSSION:

Structural Parameters:

Fig.1 shows X-ray diffraction patterns obtained for TiO2 thick films fired at 350, 450 and 5500C. In all cases, the observed peaks showed the presence of TiO2, match well with reported JCPDS data. It has been observed that the XRD peak broadening decreases with an increase of the firing temperature. The intensity of reflections increases with a rise in the firing temperature. Also XRD analysis evaluates the grain size of the thick films as function of the temperature. From this analysis all films were shown random orientation of polycrystalline nature of the material. Also for further elevated temperature surface area decreases as grain size increases hence sensitivity decreases [17]. In the field of chemical sensors, the structural stability, porosity and high surface to volume ratio are key properties for a sensing film [18].

Fig. 1: XRD pattern at different firing temperatures.



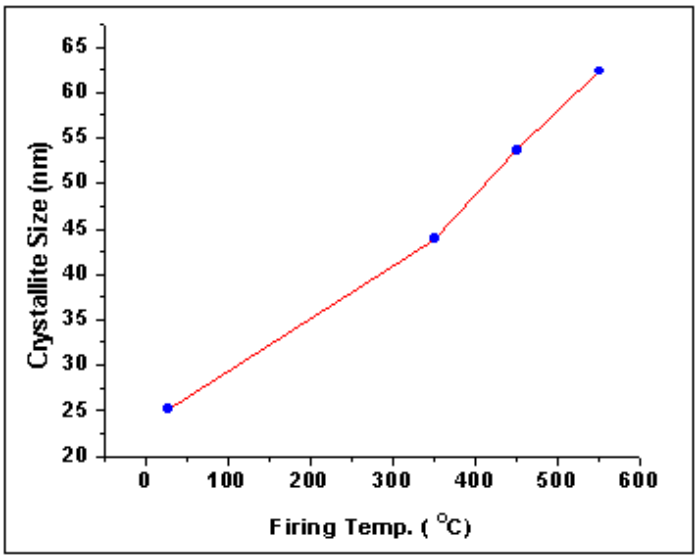
Crystallographic parameters:

The XRD pattern was used to calculate the crystallite size of TiO2films at different firing temperatures. (Scherer's formula) [19].

Table 2: Variation of structural parameters at different firing temperatures.

Firing Temp. ^{0}C	Plane (hkl)	Standard 'd' values(A^0)	Observed 'd' values (A^0)	Crystallite Size 'D' (nm)
550^{0}C	101 (A)	3.5126	3.5307	62.3517
	110 (R)	3.2456	3.2135	57.1990
	004 (A)	2.3775	2.3936	63.0599
	112 (A)	2.3299	2.3109	63.3269
	111 (R)	2.1870	2.1983	55.0538
	200 (A)	1.8900	1.8523	61.0578
	211 (A)	1.6643	1.6538	67.4669
	204 (A)	1.4794	1.4676	65.2318
	112 (R)	1.3466	1.3508	67.5880
450^{0}C	101 (A)	3.5126	3.5103	53.6064
	004 (A)	2.3775	2.4394	54.3445
	112 (A)	2.3299	2.3145	50.7278
	200 (A)	1.8900	1.8511	52.6053
	211(A)	1.6643	1.6384	54.1965
	204 (A)	1.4794	1.4576	60.7313
350^{0}C	101 (A)	3.5126	3.5501	43.8472
	004 (A)	2.3775	2.4161	37.7388
	112 (A)	2.3299	2.3133	46.2713
	200 (A)	1.8900	1.8501	43.6673
	211 (A)	1.6643	1.6691	46.8613
As deposited	101 (A)	3.5126	3.5476	25.1695
	004 (A)	2.3775	2.4162	18.6177
	112 (A)	2.3299	2.3140	21.0527
	200 (A)	1.8900	1.8502	26.2263
	211 (A)	1.6643	1.6688	31.4066

Fig. 2: Variation in crystallite size at different firing temperatures.



Elemental Composition:

The EDS spectra of TiO2 showed the major peaks which indicate the presence of titanium & oxygen only and no other impurity. The mass % of titanium & oxygen in all thick films fired at different temperature was not as per stoichiometry proportion and all thick films were observed to be the oxygen deficient and leads to conducting nature of TiO2 [21].

Table 3: Composition of TiO2 thick films.

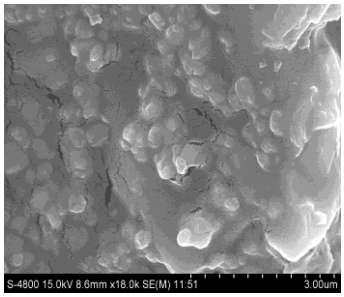
Element (Mass %)	Firing Temperature			
	As deposited	350 ^{0}C	450 ^{0}C	550 ^{0}C
Ti	67.36	78.22	79.50	83.18
O	32.64	21.78	20.50	16.82

The oxygen deficiency clearly indicates that the films are non-stoichiometry. On heating TiO2loses oxygen then titanium is excess, such oxygen deficient films would advances the adsorption of relatively large amount of oxygen species. It is very important for gas sensing applications. TiO2 thick films fired at 5500C observed the high Ti/O ratio. Therefore the optimized firing temperature 5500C selected for further studies of TiO2 thick films.

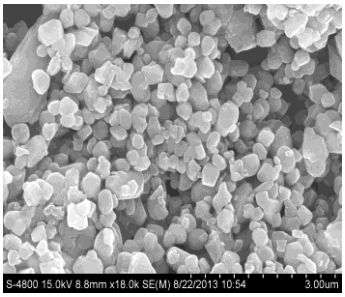
Surface Morphology Analysis:

Fig.3 (a), (b), (c) and (d) represents the FESEM images of TiO2 Thick films as deposited and fired at 350, 450 and 550 0C respectively. All the images are recorded at same magnification for comparison. The FESEM pictures clearly shown that the crystallite size increases with an increase in the firing temperature. Surface morphology has shown the particle sizes are the function of the temperature. It has been observed that an increase in the firing temperature leads to an increase in the grain & particle size which increases the mobility of atoms at the surface of the film thus decrease in surface area [20]. It can see an increase in the porosity with increase in thefiring temperature. The increase in the porous naturecan help in increasing the gas sensing performance.

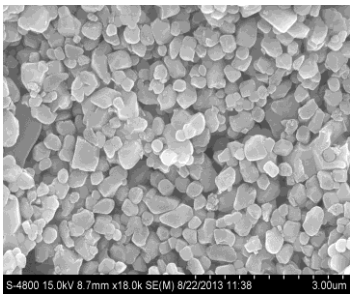
Fig. 3. FESEM of TiO2 thick films fired at (a) as deposited, (b) 350 0C, (c) 450 0C and (d) 550 0C



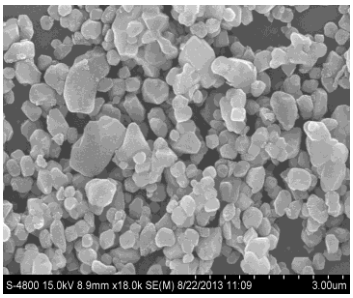
(a)



(b)



(c)



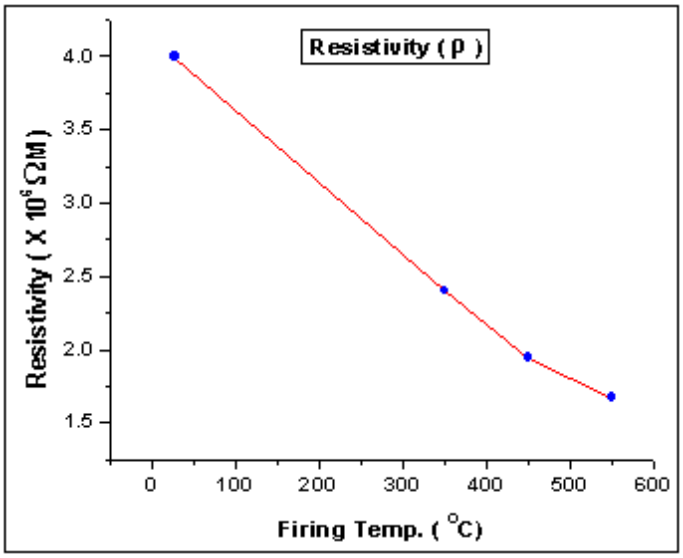
(d)

Electrical Resistivity (ρ):

Table 4: Resistivity of TiO2 thick films at different firing temperatures.

FiringTemp.(0C)	As deposited	3500C	4500C	5500C
ρ x 106(Ωm)	3.998	2.400	1.945	1.674

Fig. 4: Variation ofResistivity (Ωm) withdifferent firing temperatures.



CONCLUSIONS:

Compositional and structural analysis confirmed that TiO2 thick films were non- stoichiometry, which are suitable for gas sensing applications. The films as deposited and fired at temperatures 350, 450 and 550 0C were found polycrystalline. The crystallite size increases with an increase in the firing temperature. Films fired at 550 0C were observed to have mixed anatase-rutile structure, more crystallinity, porous, oxygen deficient and good adhesion to glass substrate. An increase in temperature improved the crystallinity and thus increased the mobility of atoms at the surface of the films.In all thick films as deposited and fired at temperatures 350, 450 and 550 0C the observed d-values well matched with standard d-values. The electrical properties were found to be function of the temperature for all TiO2 thick films.The conductivity goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the films.

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