Role of firing temperature on structural and electrical characteristics of Titania thick film for sensor applications

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Titania (TiO_2) thick films have been prepared by standard screen printing technique and subsequently fired at different temperatures (viz. 623, 723 and 823K) in air atmosphere. The role of firing temperature (FT) on various physical properties such as structural, surface morphological, compositional, electrical resistivity, Temperature Coefficient of Resistance (TCR) and activation energy have been studied. Compositional studies revealed that the thick films were oxygen deficient, indicating that they were non- stoichiometric in nature. It was observed from XRD studies that all the samples (i.e., as-deposited as well as fired) were polycrystalline in nature. Interestingly, with increase in FT the structural phase changed from anatase to a mix-phase i.e., anatase-rutile. Moreover, the effect of FT on structural parameters such as grain-size and surface-area revealed that with increase in FT, grain growth takes place, which thereby decreases the surface-area. This grain growth and increase in crystallinity with FT was equally corroborated from Field Emission Scanning Electron Microscopy (FESEM) images. Electrical property studies showed that resistance decreases with increase in temperature indicating semiconductor behavior for all the samples. Further, it is found that TiO_2 thick films have two activation energies at low and high temperature regions.

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1. Introduction

The first decade of 21st century has been labeled as “sensor decade”. It is been now well understood that the working principle of semiconductor gas sensors is based on change in electrical conductivity with the exposure of the target gases [1]. Semiconducting metal oxides (SMO) such as TiO_2, SnO_2, ZnO, Fe_2O_3, and WO_3 etc. offer the potential for developing portable and inexpensive gas sensing devices, which have advantages of simplicity, high sensitivity and fast response. TiO_2 is a widely studied transition metal oxide that behaves as n-type semiconducting oxide due to non-stoichiometry. It has been widely studied for several applications in photoelectrical, optical fields and even used as a gas sensor [2-4]. Till date, many researchers have deposited undoped as well as doped TiO_2 films in thick and thin forms by different deposition techniques such as spray pyrolysis, vacuum evaporation, chemical vapor deposition, magnetron sputtering, pulsed laser deposition, sol-gel technique, screen printing technique [2-8]. Screen printing technique [7-14] is one of the important and feasible technique that was introduced in the later part of 1950’s to produce compact, robust and relatively inexpensive hybrid circuit for many purposes. Essentially, this technique attracted thick film depositions for various different samples including oxides, which lead the foundations for a rapid progress in the field of sensors [15]. Studies related to thick films synthesized by screen printing technique demonstrated that they are rather more suitable for gas (oxygen detection) or humidity sensors for the reasons that they have good gas sensing properties due to large material surface area [16-18]. Among the various metal oxides that can be used in gas sensors, only those materials based on titanium oxide (TiO_2) have been widely manufactured and utilized [19]. In general sense, TiO_2 in thick and thin film form finds numerous applications. However, in particular sense they have very good gas sensing abilities due to the ample availability of surface oxygen absorbate species. TiO_2 can be found in three important crystalline phases: rutile, brookite and anatase [20]. TiO_2 in the anatase crystalline phase is one of the most studied materials for photo-catalysis properties as compared to the other phases [21]. The aim of the present work deals with preparation procedure of TiO_2 thick films by screen printing technique and studies related to their structural and electrical properties. Notwithstanding to this, the effect of different firing temperatures (FT) on the physical properties of TiO_2 thick films have also been studied and discussed.

2. Experimental details

2.1. Thick film preparation

Analytical Reagent (AR) grade TiO_2 powder was calcined at 673K for an hour in a muffle furnace. Then this powder was crushed and thoroughly mixed. Organic vehicles such as butyl carbitol acetate (BCA) and ethyl cellulose (EC) were added to this active material to achieve proper thixotropic properties of the paste. The ratio of inorganic to organic parts was maintained at 70:30 (the ratio of EC to BCA was 98:2 in 30 %). TiO_2 thick films were prepared on glass substrates using a standard screen-printing technique. The screen of nylon (40S, mesh no.355) was selected for screen-printing. The required mask was developed on the screen using a standard photolithography process. The paste was printed on clean glass substrates with the help of a mask. The pattern was allowed to settle for 15 to 20 minutes in air. The films were dried under infrared radiation for 45 minutes and fired at temperatures of 623, 723 and 823K for 2 h (which includes the time required to achieve the peak FT and then constant firing for 30 minutes at the peak temperature) in a muffle furnace.

2.2. Structural, morphological and compositional characterizations

The structural properties of TiO_2 films were investigated using X-ray diffraction analysis for diffraction angle $2\theta = 20\text{-}80^0$ [D-8, Advance Model, Bruker diffractometer, Berlin, Germany] with Cu-K_α radiation of wavelength λ=1.54060 Å. A Field Emission scanning electron microscopy [FESEM- X-Flash Detector S-4800 type-II, Hitachi high Technology Corporation, Japan] was employed to characterize the surface morphology. The composition of TiO_2 thick film samples were analyzed by an energy dispersive X-ray spectrometer (EDAX) [X-Flash Detector 5030, Bruker AXS GMBH]. The information about the grain shape and sizes of TiO_2 thick film materials is obtained by using FESEM. All TiO_2 samples were coated with a very thin conducting gold layer (few 100 Å) using vacuum sputtering technique to avoid charging of the samples. The composition of TiO_2 thick film samples were analyzed by EDAX.

2.3. Electrical characterization

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

$$\rho = \frac{(R \text{ x } A)}{l} \tag{1}$$

The TCR of thick film samples was calculated by the equation,

$$TCR = \frac{\Delta R}{R_0 \text{ x } \Delta T} \tag{2}$$

The activation energy of thick film samples were calculated from Arrhenius plot using the relation,

$$R = R_0 e^{-\left(\frac{\Delta E}{KT}\right)} \tag{3}$$

3. Results and discussion

3.1. Structural Parameters and their Analysis

3.1.1. XRD spectra analysis

Fig. 1 shows X-ray diffraction patterns obtained for TiO_2 thick films deposited on glass substrates and fired at 623, 723 and 823 K, respectively. All the XRD spectra obtained shows polycrystalline nature of the films. For the as-deposited and the 623 K fired sample, the respective diffraction peaks corresponding to (101), (004), (112), (200) & (211), crystal planes of anatase phase was obtained; while for 723 and 823 K apart from the above anatase phase peaks, peak corresponding to (204) crystal plane of anatase phase was also seen. In addition to this diffraction peaks (110), (111) and (112) corresponding to rutile phase was observed in the XRD spectra of film fired at 823 K indicating that at this high firing temperature there is a formation of mixed crystal planes corresponding to anatase and rutile phases. The obtained planes from the XRD data were found to be matching well with the standard reported JCPDS data card No(s). 83-2243 (Anatase) and 83-2242 (Rutile) phase of TiO_2 compound, thereby confirming the formation of TiO_2 with polycrystalline nature. The anatase and rutile phases are corresponding to tetragonal crystal structure. The most pronounced and strongly reflected peak (101) was observed at 25.2°, indicating that the crystallites prefer orientations along this particular direction, while the growth process takes place. It has been observed that with an increase of the FT there is a small uneven shift in the peak positions. Moreover, the intensity of reflections increases with a rise in the firing temperature. However, comparing the obtained intensity from the XRD patterns with the standard intensity, it was found that the films are randomly oriented; since the observed intensity of the peaks is less than the standard intensity.

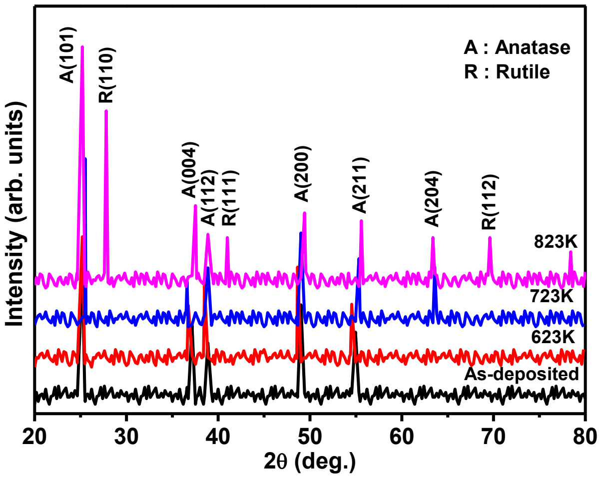

Fig. 1. XRD pattern of TiO_2 for as-deposited and fired at different FT i.e., 623, 723 and 823K.

3.1.2. Crystallite size (D) analysis

XRD spectra were used to calculate the crystallite size (D) of TiO_2 samples by using the standard Scherrer's formula [22] as given in equation 4 below:

$$D = \frac{0.9\lambda}{\beta cos\theta} \tag{4}$$

The crystallite size of TiO_2 films at different FT is as shown in fig. 2. There is an increasing trend found for the grain size of the film with an increase in the FT. The increase in the grain size may be due to the sintering of the smaller crystallites to form larger size crystallite after getting sufficient amount of thermal energy. Generally, in the field of chemical sensors, the structural stability, porosity and high surface-to-volume ratio are key properties for a sensing film [23]. Importantly, here, with increase in the FT, surface area will decrease as the grain size increases, which may drastically affect the gas sensing properties [24].

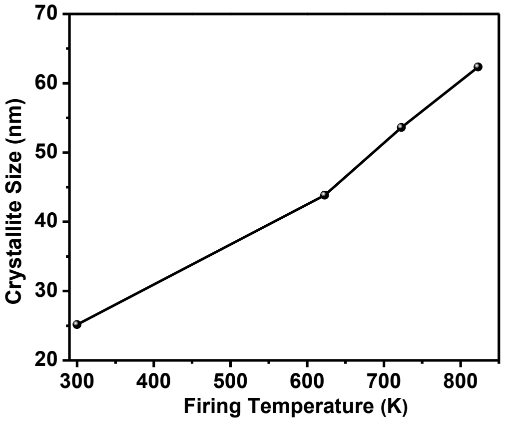

Fig. 2. Variation in crystallite size for as-deposited and fired at different FT i.e., 623, 723 and 823K.

3.2. Surface Morphology Analysis

Fig. 3 (a), (b), (c) and (d) represents the FESEM images of TiO_2 thick films as-deposited and fired at 623, 723 and 823K, respectively. All the images are recorded at same magnification for the proper and clear comparison. It is quite clearly seen that the as-deposited samples revealed nanograins embedded into an amorphous matrix; while with the increase in the FT well defined irregular shaped grains were found without any amorphous matrix. Moreover it is also seen that with increase in the FT the smaller grains coalescence together to form a bigger grain thereby increasing the grain size. This is equally corroborated with the XRD results wherein the shifting of the peak positions are observed together with increase in the crystallite size (see Fig. 2). It has been suggested that an increase in the grain size may increase the mobility of atoms at the surface of the film, which in turn decreases the surface area that may lower the gas sensitivity [25]. However, on the other hand one can see an increase in the porosity with increase in the FT [see Fig. 3 (b-d)]. Such an increase in the porous nature helps in fine diffusion of the target gas into the sample surface/interface and can help in increasing the gas sensing performance.

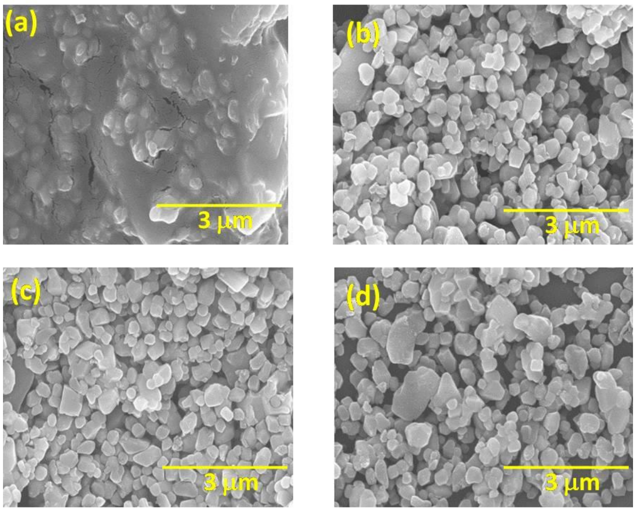

Fig. 3. FESEM of TiO_2 thick films: (a) as deposited, (b) 623K, (c) 723K and (d) 823K.

3.3. Compositional analysis

Compositional analysis done using EDAX of TiO_2 samples showed the presence of titanium & oxygen only and no other impurity (EDAX images not shown here). It was seen that the mass % of titanium & oxygen (see Table 1) in all thick films fired at different temperatures were not as per stoichiometric proportion (initially taken) and hence, all the obtained thick films were found to be the oxygen deficient leading to conducting in nature [26].

Table 1. Composition of TiO_2 thick films i.e., as-deposited, fired at FT 623, 723 and 823K.

Element (Mass %)	**Firing Temperature**			
	As deposited	623K	723K	823K
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-stoichiometric. The possible reason might be that due to heating of the TiO_2 samples; it loses oxygen, leading titanium in excess. Significantly, such oxygen deficient films would advance in the adsorption of relatively large amount of oxygen species. It is very important for gas sensing applications. TiO_2 thick films fired at 823K observed the high Ti/O ratio.

3.4. Electrical analysis

Fig. 4 represents the variation of resistance with temperature for TiO_2 thick films as deposited and fired at temperatures 623, 723 and 823K, respectively in air atmosphere. Different conduction regions such as continuous fall of resistance, an exponential fall region and saturation region were found with increase in temperature [27]. Arrhenius plot of Log R versus 1000/T for TiO_2 thick films is shown in the inset of Fig. 4.

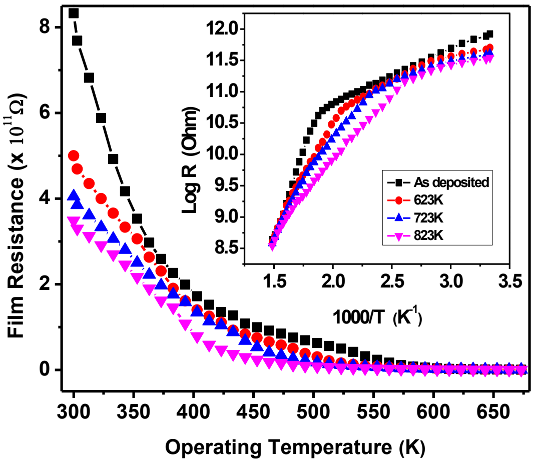

Fig. 4. Variation of film resistance versus operating temperature for the as-deposited and different FT samples (Inset: Log R versus 1000/T for as-deposited and different FT samples).

The resistivity, TCR and activation energy were evaluated from the obtained data of TiO_2 thick films i.e., as-deposited and fired at 623, 723, and 823K, respectively and is given in Table 2. The electrical resistance of these films goes on decreasing with increase in temperature. This is due to lattice vibrations or increasing drift mobility of the charge carriers, where the conduction is induced by lattice vibration and the atoms come close to each other for the transfer of the charge carriers [28]. Thus it indicates negative temperature coefficient (NTC) of resistance and shows the semi-conducting nature of the films. The film fired at 823 K shows large conductivity than other FT, because at this particular temperature, the carrier concentration increases due to intrinsic thermal excitation. Also there can be decrease in potential barrier at grain boundaries; hence the excited electrons cross over the barrier at grain boundaries [28, 29].

Significantly, the Arrhenius plot (inset of Fig. 4) shows two conduction regions one at high operating temperature region (HTR) and another low operating temperature region (LTR). The activation energy in the HTR is always higher than the LTR [30]. In LTR, activation energy decreases because small thermal energies quite sufficient to activate the charge carriers to take part in the conduction process thus the vacancies/defects weakly attached in the lattice can easily migrate. Hence, increase in conductivity in the LTR can be attributed to the increase of charge mobility. So the conduction mechanism is usually called the region of low temperature conduction. In HTR, activation energy increases because the energy needed to form the defects is much larger than the energy required for its drift. In this HTR the electrical conductivity is mainly determined by the intrinsic defects and hence is called as intrinsic conduction. Hence the intrinsic defects due to thermal fluctuations determine the electrical conductance of the films only at elevated temperature [30, 31]. Thus decrease in resistivity, TCR and activation energy is due to increase in FT of the TiO_2 thick films.

Table 2. Electrical and structural Parameters of TiO_2 thick films i.e., as-deposited, fired at FT 623, 723 and 823K.

Firing Temperature (K)	**Parameters**				
	Grain Size (D) (nm)	**Resistivity (10^6 Ω-m)**	**TCR (/ K)**	**Activation Energy (eV)**	
				HTR	**LTR**
As deposited	25.17	3.40	0.0094	1.01	0.18
623	43.85	2.40	0.0074	0.71	0.16
723	53.61	1.95	0.0070	0.58	0.12
823	62.35	1.67	0.0063	0.46	0.10

4. Conclusions

Compositional and structural analysis confirmed that TiO_2 thick films were non- stoichiometric. The films as-deposited and fired at temperatures 623, 723 and 823K were found to be polycrystalline in nature. An increase in firing temperature improved the crystallinity and thus increased the mobility of atoms at the surface of the films. Films fired at 823K were observed to have mixed anatase-rutile structure, more crystallinity, porous nature, oxygen-deficient and good adhesion to the glass substrate. The electrical properties were found to be function of the temperature for all TiO_2 thick films. Electrical resistivity measurements and negative value of TCR showed semiconducting behavior. It was found that the films fired at 823K offer low resistivity, low TCR and low activation energy. Therefore, it is confirmed that the role of firing temperature in improvement of the physical properties of TiO_2 thick films is important and can form a prerequisite step for obtaining better sensing properties.

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