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Microstructural Analysis of Screen Printed TiO₂ thick Films

C G Dighavkar^{1*}, A V Patil¹, U P Shinde¹, R Y Borse²

¹*Department of Electronic Science, L.V.H. College, Panchawati, Nasik 422003, India.*

²*Thin and Thick Film Laboratory, Department of Electronic Science, M.S.G. College, Malegaon Camp, Dist-Nasik, India.*

* cgdighavkar@gmail.com

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08000 Bechar - ALGERIA
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²Thin and Thick Film Laboratory, Department of Electronic Science, M.S.G. College, Malegaon Camp, Dist-Nasik, India.

* Corresponding author: cgdighavkar@gmail.com

Abstract – In this paper, we explore for the first time the compositional, morphological and structural properties of TiO₂ thick films prepared by a standard screen printing method and fired between 600°C to 1000°C for 2-hours in an air atmosphere. Morphological, compositional, structural properties of the samples were analyzed by scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction. X-ray diffraction shows that films are a mixture of anatase and rutile structures. During firing there was a phase transformation and at 1000 °C the anatase phase disappeared and only rutile phase was found. Scanning electron microscopy shows that the grain size increases as the firing temperature increases. From X-ray diffraction patterns the texture coefficients of (hkl) planes were evaluated which shows good crystallinity for high temperature. The crystallite size changes from 12.08 to 36.42. nm with respect to the increase in firing temperature. The dislocation density, stacking fault probability and RMS microstrain of the film were found to decrease with the firing temperature.

Keywords: TiO₂; screen printing; thick films; firing; crystallinity

I. Introduction

Titanium dioxide (TiO₂) is extensively studied because of its broad range of applications in different fields. The increased interest in both the application and fundamental research of this material in the last decade is due to its remarkable optical and electrical properties. It has high dielectric constant and high refractive index; hence it is widely used in optical coating, beam splitters and antireflection coating. It is reported on its use as gas sensor, humidity and temperature sensor (Dhage et al 2003). It is widely used in confectionery, cosmetics and food in plastic industry (Raymond et al 2002). It is investigated as key material for applications in photovoltaic cells, batteries, chemical sensing (Varghse et al 2003). Thin and thick films of TiO₂ were made by sputtering and screen printing technique for NO₂ and CO gas sensors respectively (V. Guidi et al 1999). Nano structured Nb-doped TiO₂ thick films have been prepared by screen printing process for CO gas sensors (Carrota et al 1999). Also for same doping O₂ sensitivity has been reported (Sharma et al 1999). TiO₂ behaves as semi conducting oxide due to non-stoichiometry behavior. Recently buried contact solar cells have been fabricated using TiO₂ as an optical coating. It is used as piezoelectric crystal sensor for the detection of organic vapors using nanocrystalline (Sai et al 2005). It has interesting applications in chemistry due to its behavior as a reaction catalyst (Fujisima et al 1999). TiO₂ is used as photo catalytic degradation of phenol one of the most

water pollutants (Mishra et al 2008) and environmental purification (Homyara et al 2001). Titanium dioxide occurs in nature in three crystalline forms: Anatase, brookite and rutile. These crystals are essentially pure titanium dioxide but certain amount of impurities such as iron, chromium or vanadium darkens them. Rutile is thermodynamically stable form at all temperatures and is one of the important ores of titanium (Encyclopedia of Chemical Technology).

Several deposition techniques have been developed to grow undoped and doped TiO₂ films such as spray pyrolysis evaporation, chemical vapour deposition, sol gel technique, magnetron sputtering, pulsed laser deposition and screen printing technique (Jain and Patil et al 2006; Jain et al 2006; Ansari et al 1996; Prudenziati et al 1986; Harper 1974; Jain et al 2006; Ramkumar 1986; Nimal et al 2004 and Patil et al 1998).

The aim of the present study is to prepare TiO₂ thick films by using a Standard Screen Printing Method on alumina substrates and study their structural, surface morphological and compositional properties at different firing temperature. Such a detailed understanding of the film properties is necessary if TiO₂ is to be developed to a degree which will enable its use in gas sensing devices.

II. Experimental

Analar Reagent (AR) grade TiO₂ powder was calcined at 400 °C for 2 h in a muffle furnace. Then this powder was crushed and thoroughly mixed with a glass frit (PbO-70%, SiO₂-18%, Al₂O₃-9% and B₂O₃-3%) as a

permanent binder. Organic vehicles such as butyl carbitol acetate (BCA) and ethyl cellulose (EC) were added to this mixture to achieve proper thixotropic properties of the paste. The ratio of inorganic to organic parts was maintained at 70:30 (the ratio of active powder to permanent binder was kept at 95:5 in 70% and the ratio of EC to BCA was 98:2 in 30%). TiO₂ thick films were prepared on alumina substrates using a standard screen-printing technique. The screen of nylon (40s, mesh no.355) was selected for screen-printing. The required mask (2 x 1.25 cm) was developed on the screen using a standard photolithography process. The paste was printed on clean alumina substrates (5 x 2 cm) 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 600, 700, 800, 900 and 1000 °C for 1.5 to 2 h (which includes the time required to achieve the peak firing temperature and then constant firing for 30 minutes at the peak temperature) in a muffle furnace. The structural properties of TiO₂ films were investigated using X-ray diffraction analysis from 20-80° [Rigaku diffractometer (Miniflex Model, Rigaku, Japan) with CuKα, λ=0.1542 nm radiation] with a 0.1°/step (2θ) at the rate of 2 s /step. A scanning electron microscopy (SEM-JOEL JED-2300) was employed to characterize the surface morphology. The composition of TiO₂ thick film samples were analyzed by an energy dispersive X ray spectrometer (EDS) (JOEL-JED 6360 LA). The thickness of the TiO₂ thick films was measured using a Taylor-Hobson (Taly-step UK) system. The thickness of the films was observed to be uniform in the range of 20µm to 25µm. The effect of the firing temperature on the orientation of the films was investigated by calculating the texture coefficient using the following equation.

$$T_c(hkl) = \frac{I(hkl) / I_o(hkl)}{\left(\frac{1}{N}\right) \sum I(hkl) / I_o(hkl)} \quad \text{-- (1)}$$

Where T_c (hkl) = texture coefficient of the (hkl) plane, I (hkl) = measured intensity from the (hkl) plane, I_o (hkl) = JCPDS standard intensity of (hkl) plane, N = number of diffraction peaks. The crystallite size was determined using Scherrer's formula.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{----- (2)}$$

Where D is the crystallite size, λ is the wavelength of the X-ray radiation (1.542 Å), β is the peak full width half maxima of the (101) peak of the XRD pattern and θ is the diffraction angle.

The weight fraction of rutile (W_R) can be calculated from spurr formula.

$$W_R = I_R / (0.884 I_A + I_R) \quad \text{----- (3)}$$

Where, I_A represents the integrated intensity of the anatase (101) peak, and I_R is the integrated intensity of rutile (110) peak.

The microstrain (ε) developed in the TiO₂ thick films can be calculated from the relation.

$$\epsilon = 1/2 (\beta - \lambda / D \cos\theta) / \tan\theta \quad \text{----- (4)}$$

The dislocation density (δ) was calculated using the following equation,

$$\delta = n/D^2 \quad \text{----- (5)}$$

Where n is a factor, which when equals unity giving minimum dislocation density and D is the crystallite size. The stacking fault probability was calculated using the following equation.

$$\alpha = \frac{2\pi^2 \Delta(2\theta)}{45\sqrt{3} \tan \theta_{101}} \quad \text{----- (6)}$$

The information about the crystalline shape and sizes of TiO₂ thick film materials is obtained by using SEM [Model JOEL JED-2300(LA) Germany]. For SEM all the TiO₂ samples were coated with a very thin conducting gold layer (few100Å) using vacuum evaporation/sputtering technique to avoid charging of the samples. The composition of TiO₂ thick film samples was analyzed by Energy Dispersive Spectrometer (JOEL-JED 6360 LA).Brunauer–Emmett–Teller (BET) method was applied for specific surface area evaluation and was calculated for spherical particles using the following equation.

$$S_w = 6/\rho d \quad \text{----- (7)}$$

Where d is the diameter of the particles, ρ is the density of the particles.

III. Results and Discussion

3.1 Calcinations, Drying and Firing process

The preheat treatment for the material is necessary to decrease posterior materials instabilities. During this heat treatment the materials were submitted to high calcinations temperature to avoid instabilities during their working life. The calcinations of the powder before the paste preparation and the firing process of the printed film can determine the sensitivity of the active material layer. With calcinations, grain boundaries were developed and the powder sintered to bigger agglomerations. This causes a higher surface area after firing and attains higher sensitivity to the layer (Tsolovivanov Peter 2004).

A drying stage is required to remove the organic solvents, make the printed film adhere to the substrate and be relatively immune to smudging. After printing, the film was allowed to settle in air for a few minutes so that some of the volatile solvents were evaporated slowly at room temperature. The organic agent was still present in the paste at this stage. Drying took place at temperatures between 70-180°C either in a conventional oven or by placing films under infrared radiation (Tsolovivanov Peter 2004).

The high temperature firing cycle is designed to remove the remaining organic binders, to develop the structural and electrical properties of the film and to bond the film to the substrate. Temperatures up to 1000°C are required to achieve these objectives. During this firing process the glass frit melts and grains of the functional materials are held together and also the film becomes bonded firmly to the substrate. There are three distinct regions in this firing cycle. Firstly the temperature slowly was increased towards the peak firing temperature. During this time the remaining organics were removed. This occurred at 350-400°C. As the temperature reached 600-1000°C, the glass frit softens. Secondly the temperature remained constant for about 30 minutes. During this time the active material sintered and various reactions took place. The electrical properties of the film began to develop. Finally there was a cooling stage to room temperature that allows the glass frit to solidify (Tsolovivanov Peter 2004). Softening point of glass frit is in between the temperature range 500-1000 °C (Khadayate R S 2007). Hence the minimum and maximum firing temperature range was selected 600 °C and 1000 °C respectively. Films fired at 600 °C and 700 °C did not show better adhesiveness to substrate hence these films would not be suitable for gas sensing or further applications.

3.2 Elemental Analysis

Table-1 shows the composition of the films fired at different temperatures. The EDS spectrum showed the presence of only Ti and Oxygen. From the analysis it was found that the TiO₂ films are non-stoichiometric. The deficiency or excess of any type of atom in the crystal results in a distorted band structure, with a corresponding increase in conductivity. Titanium oxide loses oxygen on heating so that Ti is then in excess. The oxygen, of course, evolves as an electrically neutral substance so that it is associated with each excess Ti ions in the crystal; there will be two electrons that remain trapped in the solid material, thus leading to non-stoichiometricity in the solid. This leads to the formation of the n-type semiconductor (San Andres et al 2005; Patil D R et al 2007). The EDS results show lot of variation Ti/O ratio with firing temperature. The mass % of Ti and O in each sample was not as per the stoichiometric proportion and all samples were observed to be oxygen deficient. Excess or deficiency of the constituent material particles leads to

the semiconducting nature of the material. It is found that high value of Ti/O ratio for TiO₂ film is at 800°C firing temperature. Therefore the TiO₂ thick film with optimized firing temperature of 800°C is chosen for further studies of pure TiO₂ samples.

Table 1: Composition of TiO₂ obtained from EDS.

Element (Mass %)	Firing Temperature		
	800°C	900°C	1000°C
Ti	60.27 %	57.63 %	59.92 %
O	39.73 %	42.37 %	40.08 %

3.3 Structural parameters and their analysis

Fig.1 shows X-ray diffraction patterns obtained for TiO₂ thick films deposited on alumina substrates and fired at 600, 700, 800, 900 and 1000 °C. In all cases, the observed peaks showed the presence of different phase of TiO₂, match well with reported JCPDS data 21-1272 and 21-1276 for anatase and rutile respectively confirming polycrystalline structure of the film. 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. The most pronounced and strongly reflected peak [101] of an anatase structure was observed at 25.8 ° and [110] of rutile structure at 28°C for the temperature 800 and 1000 °C respectively. The anatase phase transformation takes place up to 900° C, and at 1000° C no trace of anatase is observed in the XRD pattern. The intensity of anatase peak decreases as the firing temperature increases. This reduction of intensity indicates a decrease in the anatase content of the TiO₂ film (San Andres et al 2005). Up to 900° C firing temperature both the phase of anatase and rutile were observed. The intensity of anatase phase decreased at 900° C firing temperature and disappeared completely at 1000°C. This clearly indicates that phase transformation takes place up to 900°C and at firing temperature 1000°C only rutile phase was observed. The phase content of a sample can be calculated from the integrated intensities of the above-mentioned anatase and rutile peaks. If a sample contains mixture of anatase and rutile phase, the weight fraction of rutile (W_R) can be calculated from

spurr formula equation-3(Hengzhong et al 2000; Bakardjieva et al 2005; Spurr and Myers 1957; and Mardare and Rusu 2001).The intensity of the rutile peak significantly increased while that of anatase peak decreased as shown in table 2. The difference in the crystal structure in our titania powders with different anatase/rutile ratio is due to a thermal treatment at varying temperature of the anatase precipitate and spontaneous transformation from anatase to rutile. This transformation is an irreversible metastable to stable phase transition in temperature range 600–1000 °C. Same trend was reported by S. Bakardjieva et al. at different temperature and pressure conditions (Bakardjieva et al 2005).

Table 2. Weight % of anatase and rutile phase

Firing Temp. in °C	$I_{A[101]}$	$I_{R[110]}$	Anatase by XRD (W_A) %	Rutile by XRD(W_R) %
600	580	0	100	0
700	681	183	76.69	23.31
800	751	279	70.42	29.58
900	460	406	50.07	49.93
1000	0	468	0	100

Thick film fired at 800°C was shown good adhesion to the alumina substrate and dominating phase of anatase. The electrical mobility of anatase films has much larger due to the smaller electron effective mass and also the Fermi level is higher about 0.1 eV compared to the rutile structure. So these properties are useful for gas sensing and other applications. In particular, anatase TiO₂ is extensively used in gas sensing (Tank et al 1995; Gao et al 2000]. Also for further elevated temperature surface area decreases as grain size increases hence sensitivity decreases (Gao et al 2000; Sberveglieri et al 1996). In the field of chemical sensors, the structural stability, porosity and high surface to volume ratio are key properties for a sensing film (Patil et al 2007; Hadouda et al 1995).

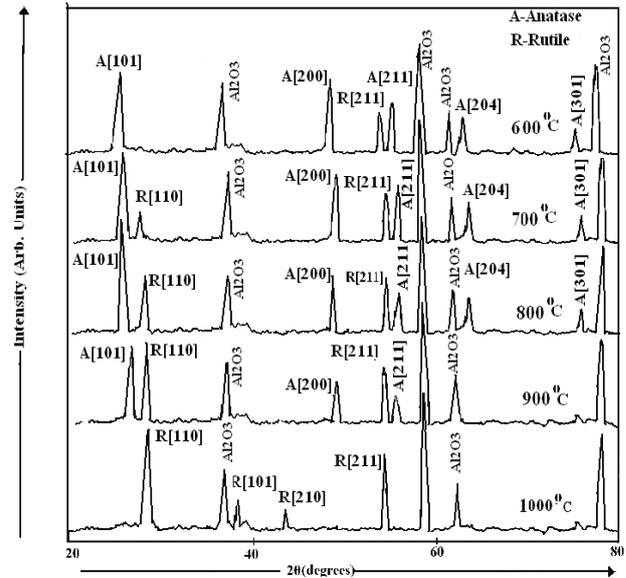


Fig.1. XRD of TiO₂ films at different firing temperatures.

3.4 Texture Coefficient (T_C)

From the values calculated using equation-1(Schuler and Aegerter 1999; Kim and Chun 1986), it was observed that T_C approaches unity for randomly distributed samples whereas T_C is larger than unity for a preferentially oriented (hkl) plane. The lower values of T_C reveals that the films have poor crystallinity and this may be improved at a higher firing temperature. The variation of the texture coefficient with firing temperatures for the A (101), A (200), A (211), A (204), A (301), R (110), R (101), R (210), and R (211) planes are in shown table 2. Also it has been observed that the preferred orientation is the A (101) plane for 600 to 900 °C and R (110) for 1000 °C for firing temperatures respectively. Film fired at 800 °C is most crystalline than films fired at other temperatures. Above this temperature anatase to rutile phase transformation takes place rapidly may be this affect on crystallinity. The increase in preferred orientation is attributed to an increased number of grains having this plane (Mahalingam et al 2007).

3.5 Crystallite size or Grain size (D)

The XRD pattern was used to calculate the crystallite size of TiO₂ by using equation-2 (Scherrer’s formula) (Cullity 1970). The crystallite size of TiO₂ films at different firing temperatures is given in Table 3. The crystallite size of the film was found to be increase with an increase of the firing temperature as shown in figure 2.

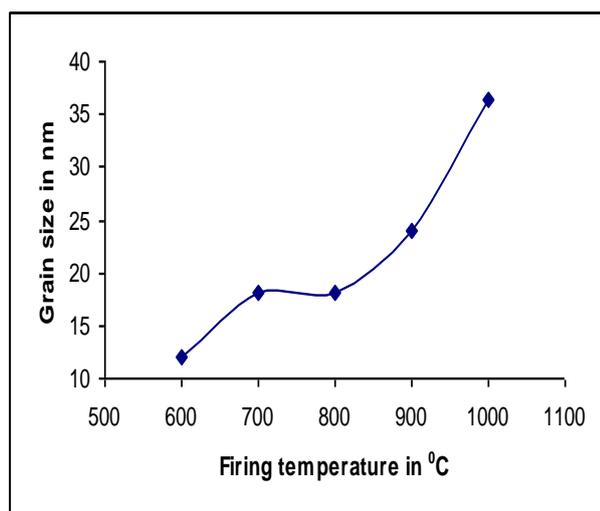


Fig.2. Variation in crystallite size with temperature.

3.6 Specific Surface Area (S_w)

The specific surface area increases as the size of the grains decreases. It was measured by the BET by using equation-7 (Gao et al 2000). The particle size increases with an increase in the firing temperature hence specific surface area decreases. The surface area of TiO₂ films at different firing temperatures is shown in Table 3.

3.7 Microstrain (ϵ)

Broadening of X-ray diffraction line profiles is mainly caused by non-ideal optics of the instrument, wavelength dispersion, and microstructural imperfections in the crystals. The microstructural line broadening can be subdivided into size broadening and strain broadening. Size broadening is due to the finite size of domains surrounded by stacking faults, by twins or other imperfections, which diffract incoherently with respect to one another. Strain broadening is caused by a varying displacement of the atoms with respect to their reference-lattice positions. A uniform compressive or tensile strain (macrostrain) results in a peak shift of the X-ray diffraction lines, whereas a uniform statistical distribution of tensile and compressive strain results in a broadening of the diffraction lines (microstrain). The microstrain was calculated by a relation given by Williamson and Hall 1953. Microstrain calculated at different firing temperatures indicate a decreasing trend with firing temperature is given in Table-3.

3.8 Dislocation density (δ)

The micro structural parameters of TiO₂ thick films fired at different temperatures are given in Table-2. The dislocation density of the TiO₂ thick films was calculated by equation-5 (Mahalingam et al 2007). A dislocation is an imperfection in a crystal associated with the misregistry of the lattice in one part of the crystal with

respect to the other part. Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections. Dislocation density was found to be decreased with increase in firing temperature as shown in table-3.

3.9 Stacking fault probability (α)

A stacking fault is a surface imperfection that arises from the stacking of one atomic plane out of sequence on another while the lattice on either side of fault is perfect. The presence of stacking fault gives rise to shift in the peak positions of different reflections with respect to the ideal JCPDS data for TiO₂ samples. From XRD pattern of TiO₂ films, peak shift $\Delta(2\theta)$ for oriented (101) plane was observed with change in firing temperature from 600 to 900 °C by an angle 0.2 °. The stacking fault probability was calculated using the equation-6 (Mahalingam et al 2007). The stacking fault probability calculated at different firing temperature is given in Table 3. From table it is seen that as the firing temperature increases stacking fault probability of the TiO₂ films decreases.

Also it was observed that the microstrain (ϵ), dislocation density and stacking fault probability (α) exhibit a decreasing trend with firing temperature, which leads to the reduction in the concentration of lattice imperfections (Williamson and Hall 1953; Karunagaran et al 2002).

3.10 Surface morphology analysis

Fig.3 (a), (b) and (c) represents the SEM images of TiO₂ Thick films fired at 800, 900 and 1000 °C respectively. All the images are recorded at 10,000x magnification for the comparison. The SEM 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. The anatase consisting of spherical particles of 200 to 300 nm dimensions where as rutile appeared as elongated rods of 2.5 μm lengths. Microstructural parameters like crystallite size and RMS strain with the firing temperature clearly shows a marginal increase up to 900 °C and beyond this temperature anatase phase disappear or transforms to rutile phase. The crystallite size of rutile phase increases rapidly at 1000 °C resulting in growth of hexagonal shaped crystallite of phase oriented at (110) plane. From the micrograph analysis it is seen that at higher temperatures polygonization of these dislocations with lowering of dislocation density at the grain boundary possibly favors the growth large sized crystallite of rutile phase [38, 39]. It has been observed that an increase in the firing temperature leads to an increase in the crystallite size and decrease in surface area. The loss in surface area available upon elevated heat treatment would affect the sensitivity (Gao et al 2000; Teleki 2006). Defect disorder is very sensitive to oxygen activity, which imposed by the gas phase during processing of

TiO₂ at elevated temperatures. The firing increases the atomic mobility; the atoms can be moved to more energetically favoured sites such as voids, grain boundaries and interstitial positions. An increase in temperature improves the crystallinity and thus increases the mobility of atoms at the surface of the films (Bak et al 2007).

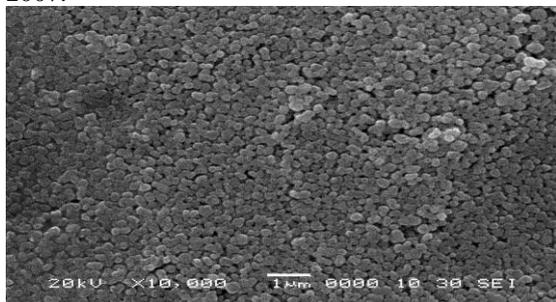
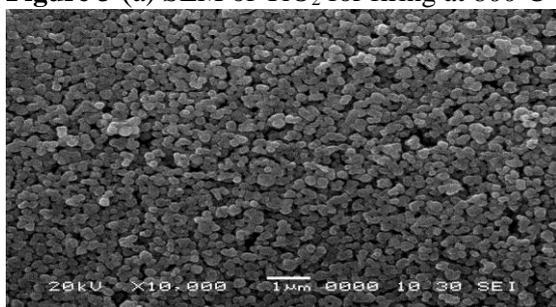
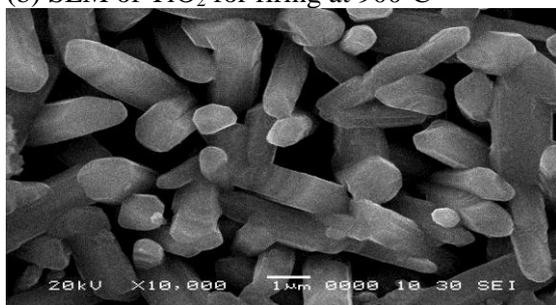


Figure 3 (a) SEM of TiO₂ for firing at 800°C



(b) SEM of TiO₂ for firing at 900°C



(c) SEM of TiO₂ for firing at 1000°C.

Table 3: Microstructural Parameters of TiO₂ films fired at different temperatures

Firing Temp. in °C	Crystallite (Grain) Size (D) In nm	Texture Coefficient	Dislocation Density $\times 10^{11}$ δ (cm ⁻²)	Microstrain (e)	Stacking fault Probability (e)	Surface Area (S _w) m ² /g
600	12.08	2.027	6.8520	1.5377	0.010	8.56
700	18.07	2.36	3.0625	1.0170	0.006	8.11
800	18.08	2.46	3.0557	1.0090	0.002	7.71
900	23.94	1.16	1.7448	0.7568	0.001	5.50
1000	36.42	1.39	0.7539	0.4625	0	1.41

IV. Conclusion

TiO₂ thick films were prepared on alumina substrate by standard screen printing technique which is simple and an inexpensive method. From EDS and SEM it was confirmed that TiO₂ films were non-stoichiometric, which are suitable for gas sensing application. The films fired in

the temperature range of 600–1000°C, were found polycrystalline. Films fired at 600 °C and 700 °C did not show better adhesiveness to substrate hence these films will not be suitable for gas sensing or further applications. Transformation of anatase phase to rutile phase was found up to 900 °C. At 1000°C only rutile phase was found. The grain size increases with an increase in the firing temperature hence specific surface area decreases. Film fired at 800 °C observed optimum surface area than further elevated temperatures. Film fired at 800 °C was shown more crystalline, porous, oxygen deficient, optimum specific surface area and good adhesion to alumina substrate. The film fired at this temperature may be suitable candidate for sensing applications. The microstrain, dislocation density and stacking fault probability of the film were decreased with an increase of the firing temperature, leading to the reduction in the concentration of lattice imperfections. The firing increases the atomic mobility; the atoms can be moved to more energetically favoured sites such as voids, grain boundaries and interstitial positions. An increase in temperature improves the crystallinity and thus increases the mobility of atoms at the surface of the films.

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P.O.Box 417 route de Kenadsa

08000 Bechar - ALGERIA

Tel: +213 (0) 49 81 90 24

Fax: +213 (0) 49 81 52 44

Editorial mail: jrs.bechar@gmail.com

Submission mail: submission.bechar@gmail.com

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