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ORIGINAL ARTICLE

Electrical investigation of TiO_2 thin films coated on glass and silicon substrates—effect of UV and visible light illumination

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Abstract The conducting nature of nanocrystalline TiO_2 thin film coated on glass and silicon (Si) substrates was studied in detail. The films were prepared through sol–gel spin-coating method with variation in coating parameters viz, the thickness of the film and the post annealing temperature. The thickness of the films was measured using Stylus profilometer. The resistivity of the film, as a function of film thickness, under the illumination of UV, visible light, and dark conditions was found using the four-probe method. The results show that the resistivity of the film decreases with increase in thickness of the film. The decrease in resistivity of the film is attributed to increase in cross-sectional area and rearrangement and removal of defects. Illumination of the samples under visible and UV light further decreases the resistivity of the film. The electrical resistivity of TiO_2 film coated on Si substrate was observed to be lesser than that of the glass substrate.

Keywords TiO_2 thin films · Glass and silicon substrates · XRD · Electrical properties · Light illumination

Introduction

Titanium dioxide (TiO_2) is a widely recognized candidate for photovoltaic (PV) applications because of its photoactive and electrical properties (Chien-Tsung Wang et al. 2013). TiO_2 is a large band gap (3–3.2 eV) semiconductor with remarkable electrical and optical properties such as high refractive index, good transmission in the VIS and NIR regions, and high dielectric constant (NarasimhaRao 2002). TiO_2 thin film coated on glass substrate finds application in sensors, water splitting, MOS capacitor, and Dye-sensitized solar cells (Shinde et al. 2008). TiO_2/Si structures constitute a primary component in the fabrication of photovoltaic and optoelectronic devices and recent research has paid special attention to the search for novel appropriate techniques to enhance their efficiency (Arun Kumar et al. 2013). TiO_2 thin film was generally prepared by sol–gel spin-coating method for its good film homogeneity, low processing temperature, large area coating, and low equipment cost (Hazra et al. 2013). The present work deals with the electrical investigation of TiO_2 thin film coated on glass substrate under dark condition and under illumination of UV and visible light at room temperature. TiO_2 is a good *n*-type partner to form heterojunction with *p*-type Si. This *p*–*n* heterojunction system is widely investigated for solar cell application. So, in the present work, *n*-TiO_2 film was also coated onto *p*-Si substrate and its electrical investigations were done.

Experimental details

In the present study, TiO_2 thin film was prepared using titanium tetra isopropoxide (TTIP) by sol–gel spin-coating method. 1 ml of TTIP was mixed with 10 ml of ethanol and stirred for 10 min using a magnetic stirrer to obtain a milky white solution. To this mixture, 1 ml of acetylacetone was added and stirred for 30 min. Again, 10 ml of ethanol was added to the solution and stirred vigorously for 3 h. The prepared sol was kept in open air for 48 h for aging to form the gel. The gel was dropped onto the cleaned substrates of

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glass and *p*-type silicon wafer, which were rotated at a speed of 3000 rpm for 10 s by using a spin coater. The coated layer was dried at 150 °C for 10 min in a muffle furnace. The process of spinning and drying was repeated for two more times to obtain a three-coating film. Finally, the coated films were annealed at 450 °C for 1 h. Two more films of five and eight coatings were also prepared. Similarly, three, five, and eight layer coated films with a post annealing temperature of 550 °C were also synthesized. The thickness of the films was measured using Surfest SJ-301 Stylus profilometer. XRD study of TiO_2 films was done using X'PertPro X–ray diffractometer, which was operated at 40 kV and 30 mA with $CuK\alpha_1$ radiation of wavelength 1.5407 Å. UV–visible spectra were recorded in the range of 200–800 nm by using the Schimadzu 1800 UV–VIS–NIR spectrophotometer. Resistivity study of TiO_2 thin film was done using Four-probe set-up, SES instruments model CCS-01 constant current source.

Results and discussion

XRD patterns of TiO_2 thin films coated on glass substrates annealed at 450 and 550 °C are shown in Fig. 1a, b respectively. Figure (2a–f) shows the XRD patterns of TiO_2 films coated on Si substrate.

The observed XRD patterns show that the coated films have a tetragonal structure comprising anatase and rutile phases. The dominant (101) peak present at $\sim 25^{o}$ corresponds to the anatase phase (JCPDS-21-1272), and the (211) peak at $\sim 54^{o}$ corresponds to the rutile phase (JCPDS-21-1276). The XRD patterns of TiO_2/Si show a much dominant Si peak at $\sim 68^{o}$.

The size of the particles present in TiO_2 thin film was calculated using the Debye–Scherrer formula,

$$D = k\lambda/(\beta \cos\theta), \tag{1}$$

where D particle size (nm), k shape factor (0.94), λ wavelength of the incident X-ray beam in Å, $\beta \rightarrow$ full width at half maximum (FWHM) of the prominent peak, and $\theta \rightarrow$ diffraction (Bragg) angle.

The dislocations are imperfections in a crystal and are important in growth mechanism. The dislocation density δ represents the amount of defects in the film which can be determined using the formula,

$$\delta = 1/D^2, \tag{2}$$

where δ dislocation density (lines/m^2) and D grain size (nm) which was calculated from Debye–Scherrer formula.

Table 1 shows the values of thickness, particle size, and dislocation density of TiO_2 thin films coated on glass and Si. From Table 1, it can be seen that the film thickness and the particle size increase and the dislocation density decreases with increase in number of coatings and also with annealing temperature. A lower value of δ shows improvement in the crystallinity of TiO_2 films.

In the present work for the same number of coatings, the thickness of the films varies for the Glass and Silicon substrates (Table 1). This may be due to the fact that nature and the finish of the substrate surface will have considerable effect on the deposited layers (Goswami 1996). In addition, the adhesiveness of the gel over different substrate surfaces can also be a cause for the varying thickness of the films formed over the surfaces.

The percentage of anatase and rutile phases of the films was calculated from XRD data using the following equations (Klu and LE Alexander 1954)

$$\text{Anatase } (\%) = \left[\frac{0.79I_A}{(I_R + 0.79I_A)}\right] \times 100 \tag{3}$$

$$\text{Rutile } (\%) = \left\{\frac{1}{\left[\frac{I_R + 0.79I_A}{(I_R)}\right]}\right\} \times 100 \tag{4}$$

where I_A and I_R are the peak intensities of (101) and (211) reflections of anatase and rutile phases, respectively.

Figure 3a, b shows the bar diagram representation of the percentage of anatase and rutile phases of TiO_2 films

Table 1 Thickness, particle size, and dislocation density of TiO_2 thin films coated on glass and silicon

Substrate	Number of coatings	Thickness (μm)		Particle size (nm)		Dislocation density (lines/m^2)	
		(450 °C)	(550 °C)	(450 °C)	(550 °C)	(450 °C)	(550 °C)
Glass	3	0.54	0.71	6	7	0.0250	0.01800
	5	0.90	1.34	8	19	0.0150	0.00280
	8	1.50	1.74	13	85	0.0064	0.00014
Silicon	3	0.24	0.52	15	28	0.0044	0.00130
	5	0.66	0.72	20	30	0.0025	0.00110
	8	1.36	1.65	22	32	0.0020	0.00090

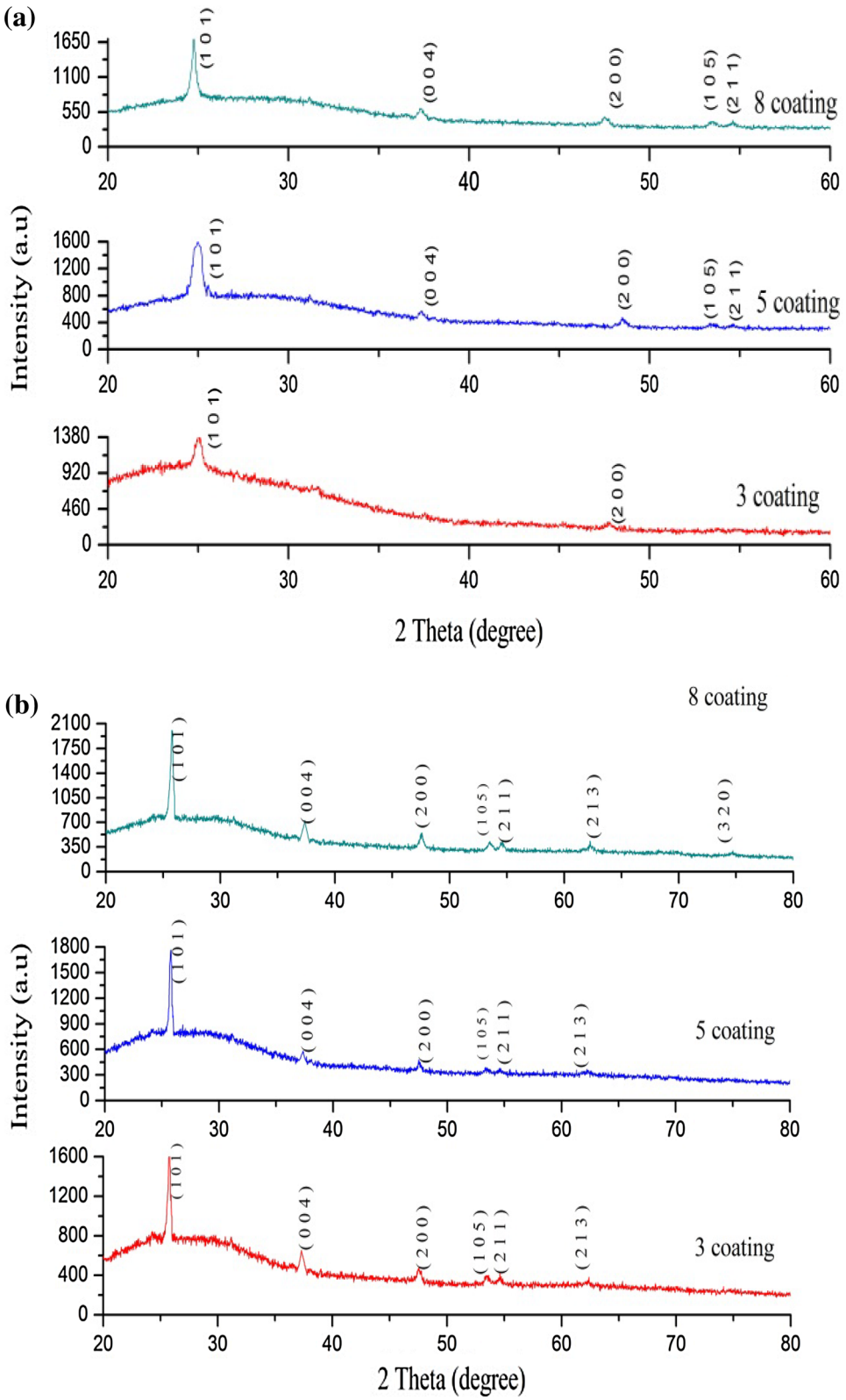

Fig. 1 XRD patterns of TiO_2 thin films coated on glass annealed at **a** 450 °C and **b** 550 °C

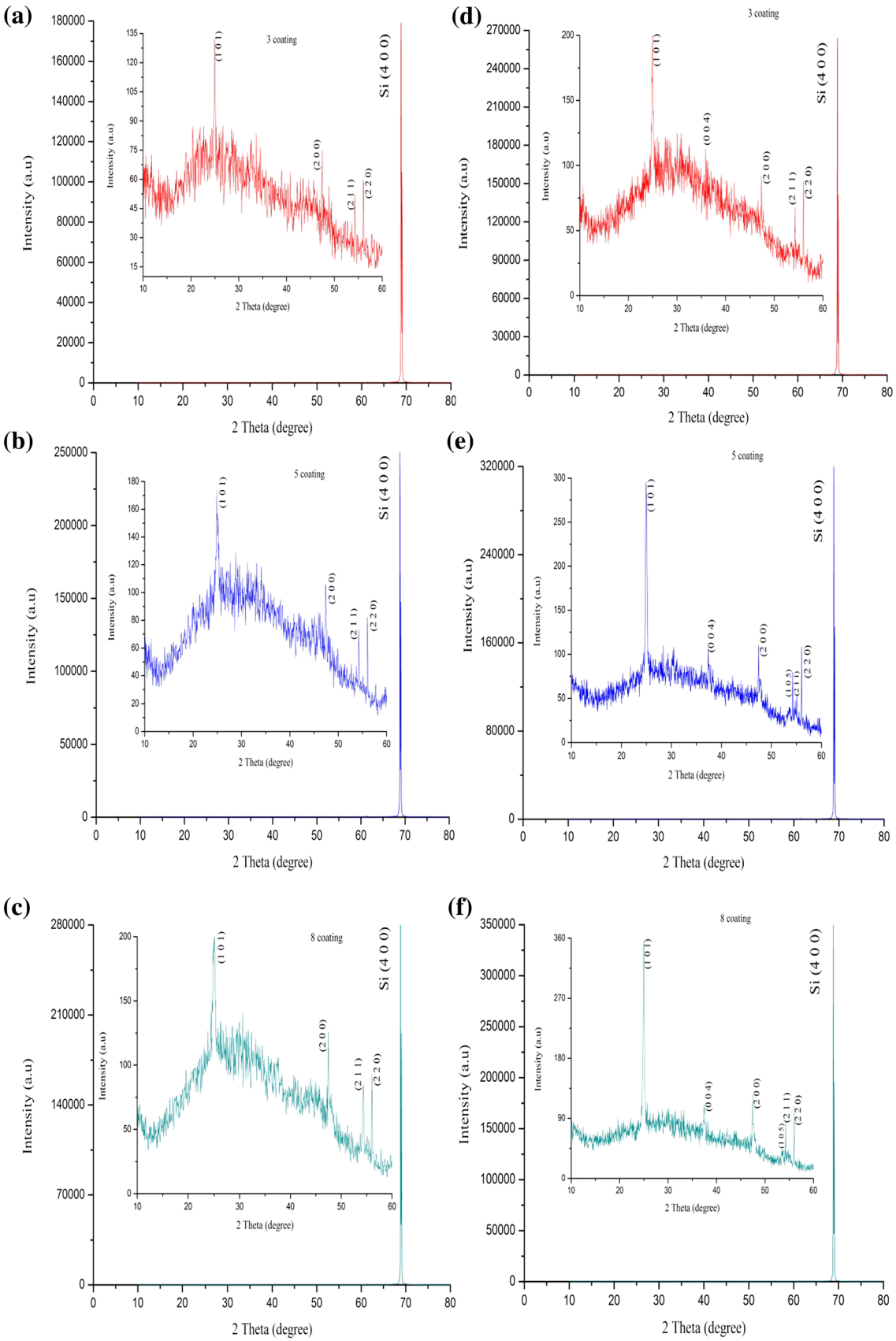

Fig. 2 XRD patterns of TiO_2 thin films coated on Si annealed at **a**–**c** 450 °C and **d**–**f** 550 °C

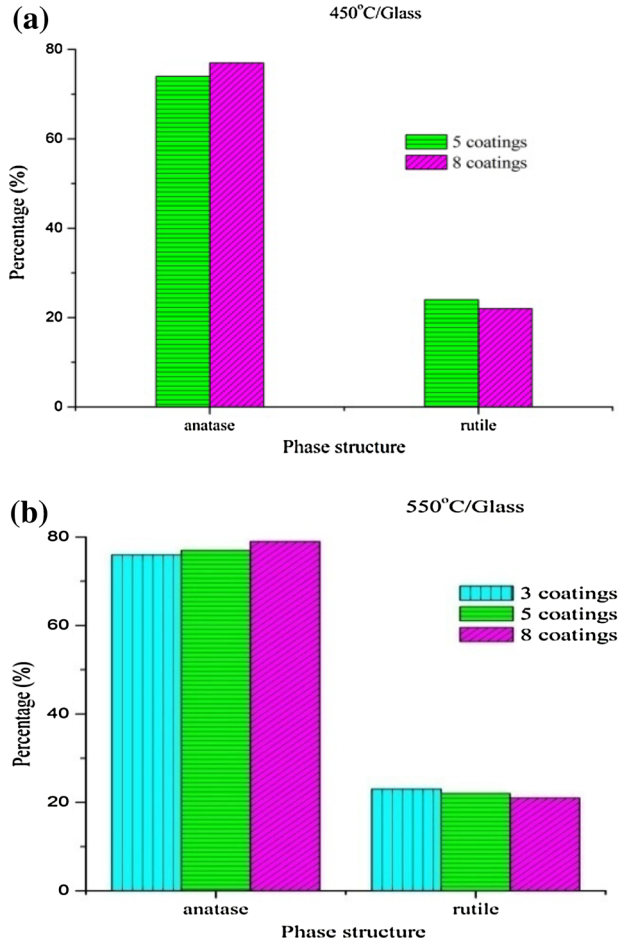

Fig. 3 Percentage of anatase and rutile phases of TiO_2 coated on glass annealed at **a** 450 °C and **b** 550 °C

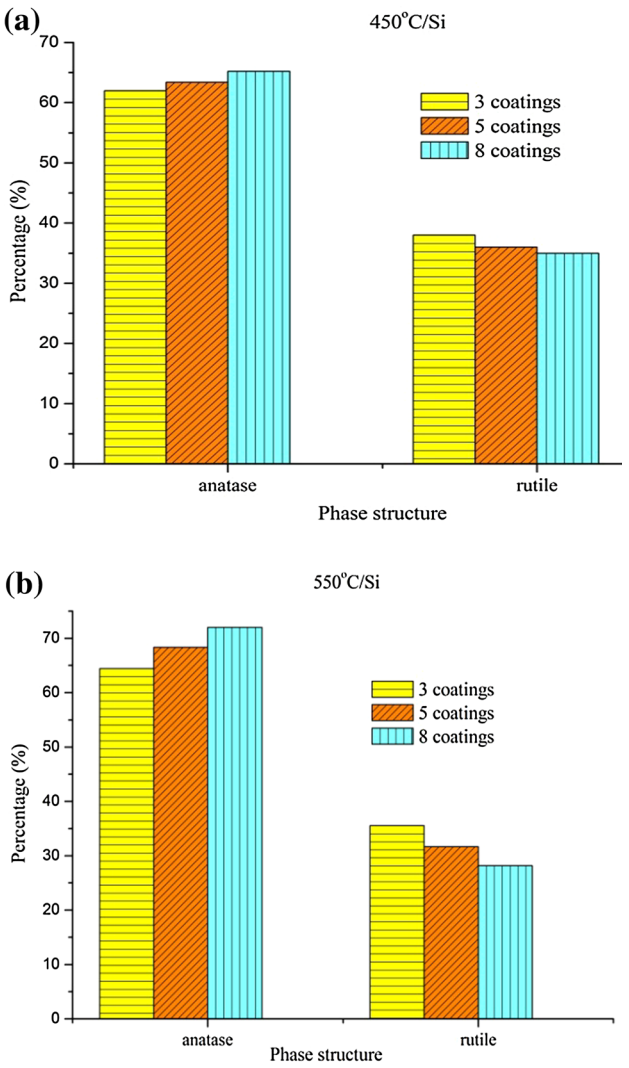

Fig. 4 Percentage of anatase and rutile phases of TiO_2 coated on Si annealed at **a** 450 °C and **b** 550 °C

coated on glass. The rutile phase is absent for the three-coating film coated on glass at 450 °C.

Figure 4a, b shows the bar diagram representation of the percentage of anatase and rutile phases of TiO_2 film coated on Si.

From these bar diagrams, it is observed that the percentage of anatase phase is found to increase and the percentage of rutile phase is found to decrease with the increase in the film thickness.

Figure 5a, b shows the UV–visible transmittance spectra of TiO_2 thin films coated on glass annealed at 450 and 550 °C, respectively. From UV–visible plots, it is observed that the optical transmittance is found to decrease as the film thickness increases. The transmittance in the visible region was observed to be maximum for the film annealed at 550 °C with three coatings and also all the films annealed at 550 °C has better transparency than the films annealed at 450 °C.

The type of electrical conduction was found to be *n*-type for these TiO_2 thin films as verified by the hot-probe technique.

Electrical measurements as a function of film thickness were made for the films coated on glass and Si substrates by four-probe method at room temperature.

The Four-probe method is one of the standard and most widely used methods for the measurement of resistivity. In this method, the current is passed through the two outer probes and the voltage is measured across the two inner probes. In the present work SES instruments (model CCS-01) constant current source was used.

The electrical resistivity of the transparent conducting oxide (TCO) thin films strongly depends on several factors such as rate of deposition, thickness, temperature, and purity (Oja et al. 2004; Yildiz et al. 2010). The intrinsic defects, more precisely oxygen vacancies, can be attributed to the electrical conductivity of metal oxides and the presence of a large number of defects around boundaries strongly affects the motion of charge carriers (Wittmer

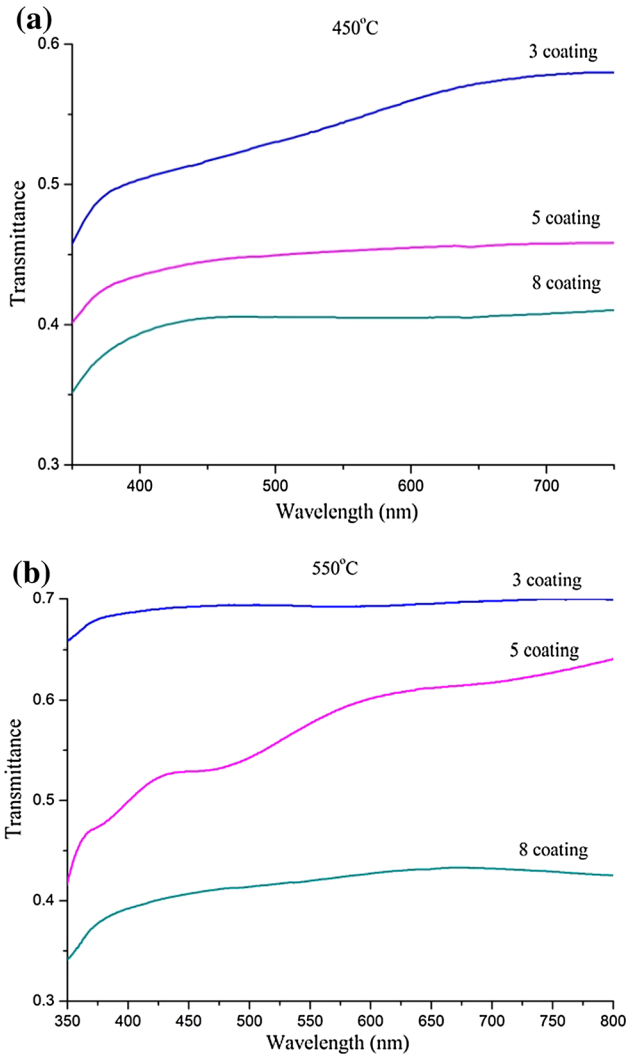

Fig. 5 UV transmittance spectra of TiO_2 thin film coated on glass annealed at **a** 450 °C and **b** 550 °C

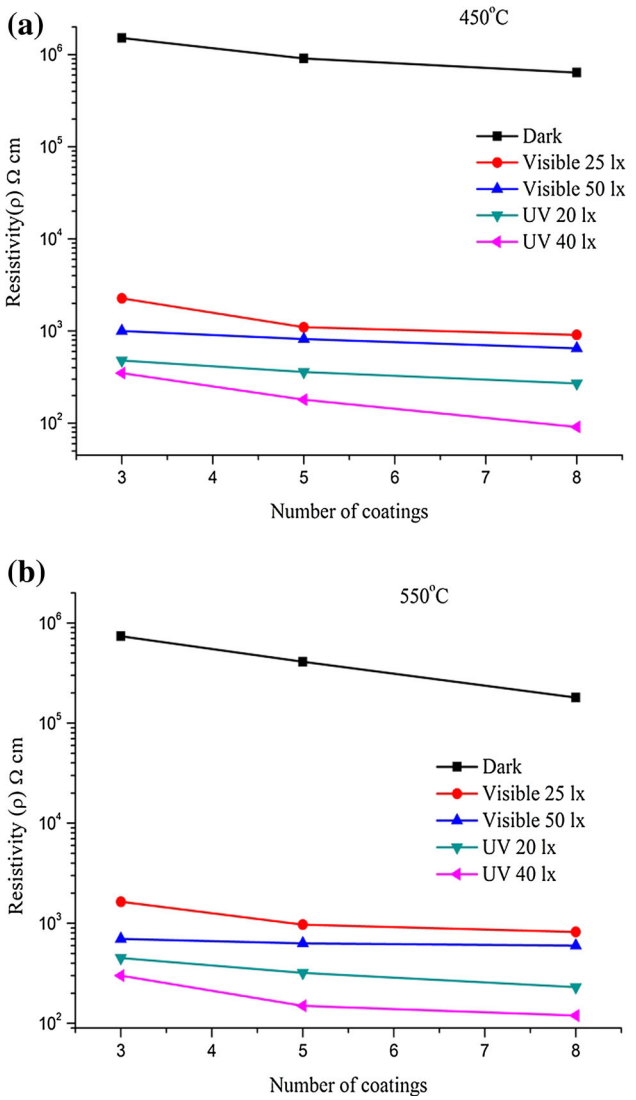

Fig. 6 Resistivity plot for the TiO_2 films coated on glass annealed at **a** 450 °C, **b** 550 °C under various illuminating conditions

et al. 2000). These defects act as traps for the free charge carriers and thereby reduce the electrical conduction. The photoelectrical properties of the TiO_2 thin films under visible and UV light irradiation were measured for the samples. When TiO_2 material is excited by the UV light having the photon energy equal to or greater than the TiO_2 band gap, electron–hole pairs are created and the electrons are promoted from the valence band to the conduction band leaving positive holes in the valence band. If the electrons and holes do not recombine they can undergo charge transfer processes such as reductive and oxidative reactions on the material surface (Linsebigler et al. 1995; Skubal et al. 2002).

The resistivity of the thin films was found using the formula

$$\rho = \frac{\rho_o}{G_7\left(\frac{W}{S}\right)} \tag{5}$$

and

$$\rho_o = \frac{V}{I} \times 2\pi S, \tag{6}$$

where ρ—resistivity, the function, $G_7(W/S)$ is a divisor for computing resistivity which depends on the value of W—thickness of the film, and S—distance between the probes.

Figure 6a, b shows the resistivity plots of the TiO_2 films coated on glass and annealed at 450 and 550 °C, respectively, under different illumination conditions. The resistivity of the film calculated from the four-probe method was found to be in a range of mega ohm cm (MΩ cm) under the dark condition for the films. The high value of resistivity may be due to the chemisorptions of a large number of oxygen molecules at the surface grain boundaries (Joseph et al. 1999).

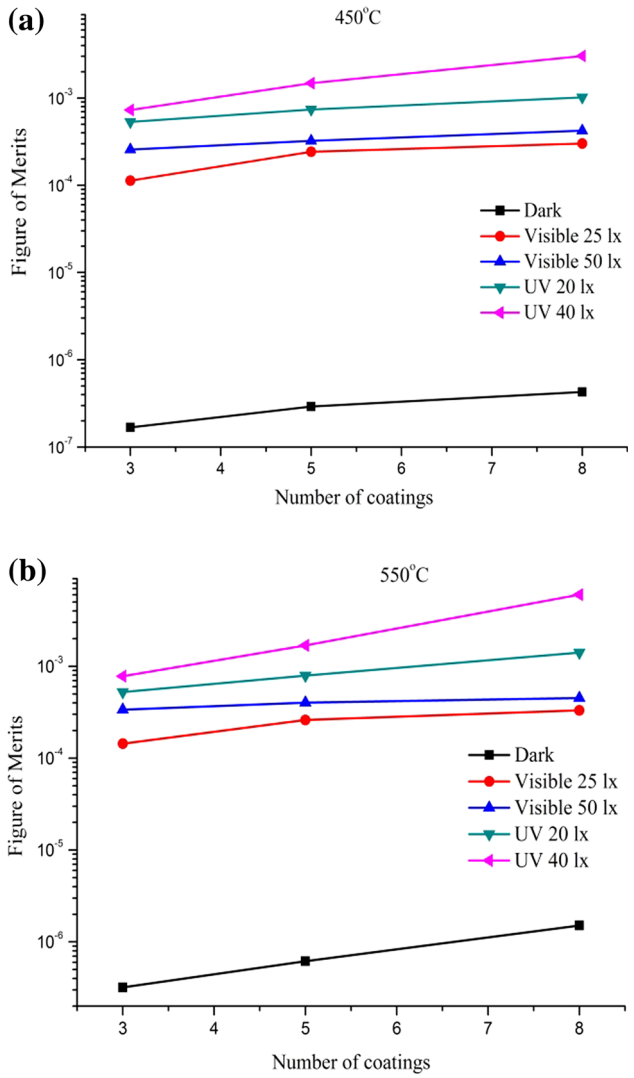

Fig. 7 Figure of merit plot for the TiO_2 films coated on glass annealed at **a** 450 °C and **b** 550 °C under various illuminating conditions

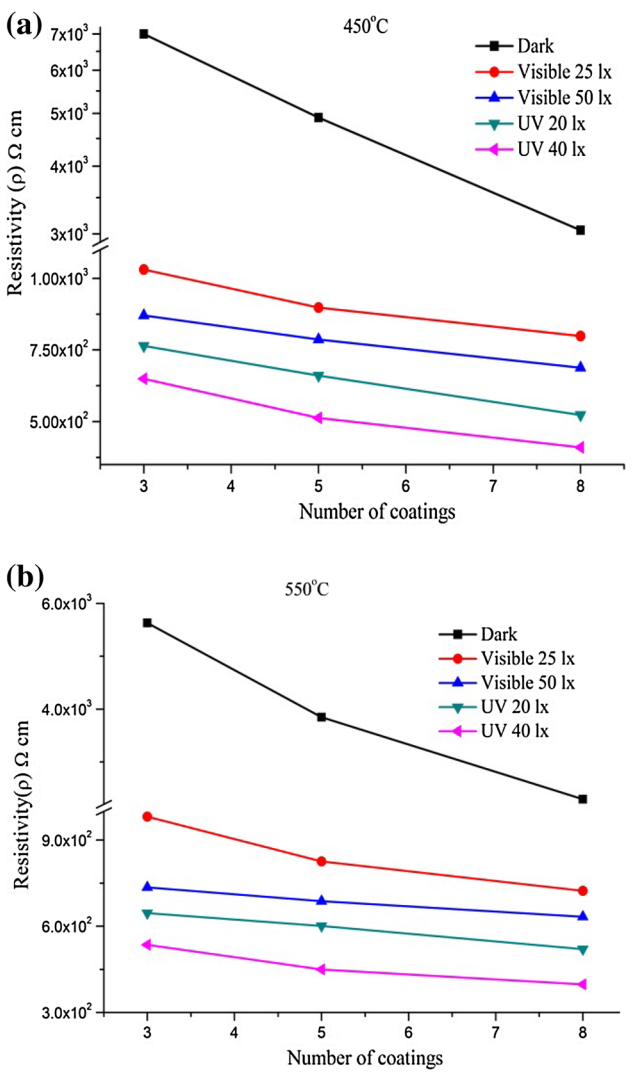

Fig. 8 Resistivity plot for the TiO_2 films coated on Si substrate annealed at **a** 450 °C and **b** 550 °C under various illuminating conditions

In order to study the resistivity of the films under illumination, the samples were illuminated with visible and UV lights. The resistivity drastically falls to the range of ohm cm under the light illuminations. From Fig. 6a, b, it can be observed that the resistivity decreases with increase in number of coatings.

The high value of resistivity in dark condition may be due to the lower density of the free charge carriers within the material or due to the high barrier height at grain boundaries, or by a combination of both. The film has higher electrical resistivity under dark condition.

Devices using transparent conductors require high electrical conductivity and optical transmission. Scropp suggested a Figure of merit (F) which is a combination of electrical (resistivity) and optical (transmittance) property. It has been observed that the performance of such devices has improved as high as the values obtained for F, given by

$$F = \frac{1}{\rho \ln T}, \tag{7}$$

where F—figure of merit, ρ—resistivity of the film, and T—transmittance of the film.

Figure 7a, b shows the Figure of merit plots of the TiO_2 films coated on glass and annealed at 450 and 550 °C, respectively. From Fig. 7a, b, it was observed that the figure of merit was low, under dark condition. Illuminating with the visible and UV light shows a rise in the figure of merit of the samples.

Figure 8a, b shows the resistivity plots of the TiO_2 films coated on Si annealed at 450 and 550 °C, respectively. The

calculated resistivity value was at a range of kilo ohm cm (KΩ cm) for the films coated on Si. The high value of resistivity was observed in the film with three coatings annealed at 450 °C under the dark condition.

For both glass and Si substrates, the resistivity of the film decreases with increase in film thickness. The fall of resistivity may be associated with rearrangement and removal of point defects and also increase in cross-sectional area.

From Figs. 6 and 8, it can be observed that the resistivity values of the films found to decrease with increase in intensity of both visible and UV light sources. The decrease in resistivity can be attributed to generation of more electrons and holes with increase in intensity of visible and UV light sources. The presence of structural defects in the TiO_2 thin film may be also a cause for generation of more free electrons with increase in intensity impinging light.

Conclusion

The TiO_2 thin films were coated on glass and Si substrates and their structural and electrical properties were studied. The percentage of anatase and rutile phases of TiO_2 thin film coated on glass and Si substrates was calculated from XRD data. The photoelectrical properties of the TiO_2 films coated on glass and Si substrates were studied by applying four-probe method under dark, visible, and UV illumination. Figure of merit which is a combination of optical and electrical properties was measured for TiO_2 films coated on glass substrates. For the films coated on glass and Si substrates, the resistivity was found to decrease with increase in number of coatings and annealing temperatures. It could be concluded from the present study that *n*-TiO_2/*p*-Si structure under the light illumination can be probably used for photovoltaic applications.

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