TEMPERATURE DEPENDENT CHARACTERIZATION OF AL DOPED TiO_2 PARTICLES

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Abstract

The research describes the structural and optical properties of Aluminium Al_x, $TiO_{2\ (1-x)}$(Al 5, 10 and 15 wt %) doped Titanium dioxide thin films prepared by thermal diffusion technique. The Aluminium and Titanium dioxide mixed samples are annealed in temperature controller furnace at different temperature scale for each sample are 400°C, 500°C, 600°C, 700°C and 800°C for two hours. The samples are characterized by X-ray diffraction technique (XRD). The band gap energy of all doped sample are studied by Ultra-Violet visible absorption spectroscopy (UV-Vis). The surface morphology and grain size of samples are measured by Scanning Electron Microscopy (SEM). X-ray diffraction result reveal the tetragonal structure of samples with secondary phase formation changed depend on increasing temperatures. The Ultra-violet visible absorption spectroscopy studies Aluminium doped Titanium dioxide show the band gap differs from Titanium dioxide anatase form. The Aluminium doped Titanium dioxide samples are deposited on glass and p-type Si (100) substrates by screen printing method. The Aluminium doped Titanium dioxide deposited on glass thin films are heating temperature 200°C for 30 minutes. The Aluminium doped Titanium dioxide deposited on p-type Si substrate thin films are heating temperature 300°C to 800°C for one hour.The electrical properties of Aluminium doped Titanium dioxide deposited on glass and Si substrate thin films are measured by standard electrical devices.

Introduction

TiO_2 is one of the most commonly used semiconductors in photocatalytic and photovoltaic applications because of its different properties, such as low cost, low toxicity, chemical stability, and so on. It is used in photovoltaic application as a semiconductor in dye-sensitized solar cells (DSSCs). Doping TiO_2 is an interesting strategy used to improve its properties as a semiconductor and, thus, its efficiency in many applications. However, only a few studies on the doping of TiO_2 with Alhave been

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performed, and in these cases, the percentage of doping was low, at around (5,10 and 15wt%) in Al doped TiO_2, which is 15wt%,the maximum doping obtained by using dissolution methods for synthesis. Al doped TiO_2particles were synthesized by using two methods (named methods: Thermal Diffusion method and Co-precipitation method) to produce levels of doping(5,10 and 15wt%) while maintaining the crystallinity of the samples in most cases. The synthesized samples were extensively characterized through XRD methods, which enabled the study of the characteristic and phase changes as a function of the annealing temperature, the percentage of doping, and the method of synthesis used. With both methods of synthesis, the formation of the rutile phase was display of the doping was increased, so the anatase phase was predominant in most cases.

Experimental Procedure

Sample Preparations

TiO_2 powder and Al powder are used as starting material for Al doped TiO_2. The first method synthesis of Al powder and TiO_2 powder were mixed by Al powder of weight ratio (5, 10 and 15 wt%) and Al is x and TiO_2 powder is (1-x) ratios are stirred with ceramic mortar for two hours as shown in Figure-1 to 5. The mixtures of Al doped TiO_2 powders were heated at 400°C to 800°C for two hours by thermal diffusion method. The second method of the Al doped TiO_2 samples have been prepared by co-precipitation method are as shown in Figure 6 and 7. Analytical grade of pure TiO_2, the various ratio of aluminium nitrate $Al(NO_3)_3.9H_2O$ are used as a main chemicals and ammonia and distilled water (DI) were used as agent materials. In a typical experiment were dissolved of distilled water (DI) in TiO2, aluminium nitrate $Al(NO_3)_3.9H_2O$ and ammonia(drop by drop) stirring for two and half hours with heated temperatures 150°C then the white precipitation powder were drop on the bottom of the flask. The mixture powder was filtered and the white solid was collected and washed several times with distilled water (DI) and ethanol as shown in Figure-4.After washing process, for precipitation of the final samples were dry in air for 120 hours and calcine temperature is 600°C for 2 hours in furnace. The final samples doped TiO_2 with Al concentrations are (5, 10 and 15 wt%) respectively by using co-precipitation

method. In these two process, the best ratio of Al doped TiO_2 powder were placed into the beaker and mixed with 2-methoxyethanol, propylene glycol (PPG) and stirred homogeneously for 1 hour. After that Al doped TiO_2 solvent were obtained to use for deposited on glass and silicon substrates. The p-type silicon (100) and glass substrates were cleaned with standard process and used for the deposition of the Al doped TiO_2 solvent by screen printing method. Finally, Al doped TiO_2 deposited on Si thin films were annealed at different temperatures for 300°C to 800°C.The electrical properties of Al doped TiO_2 deposited on Si thin films were examined by standard electrical equipment.

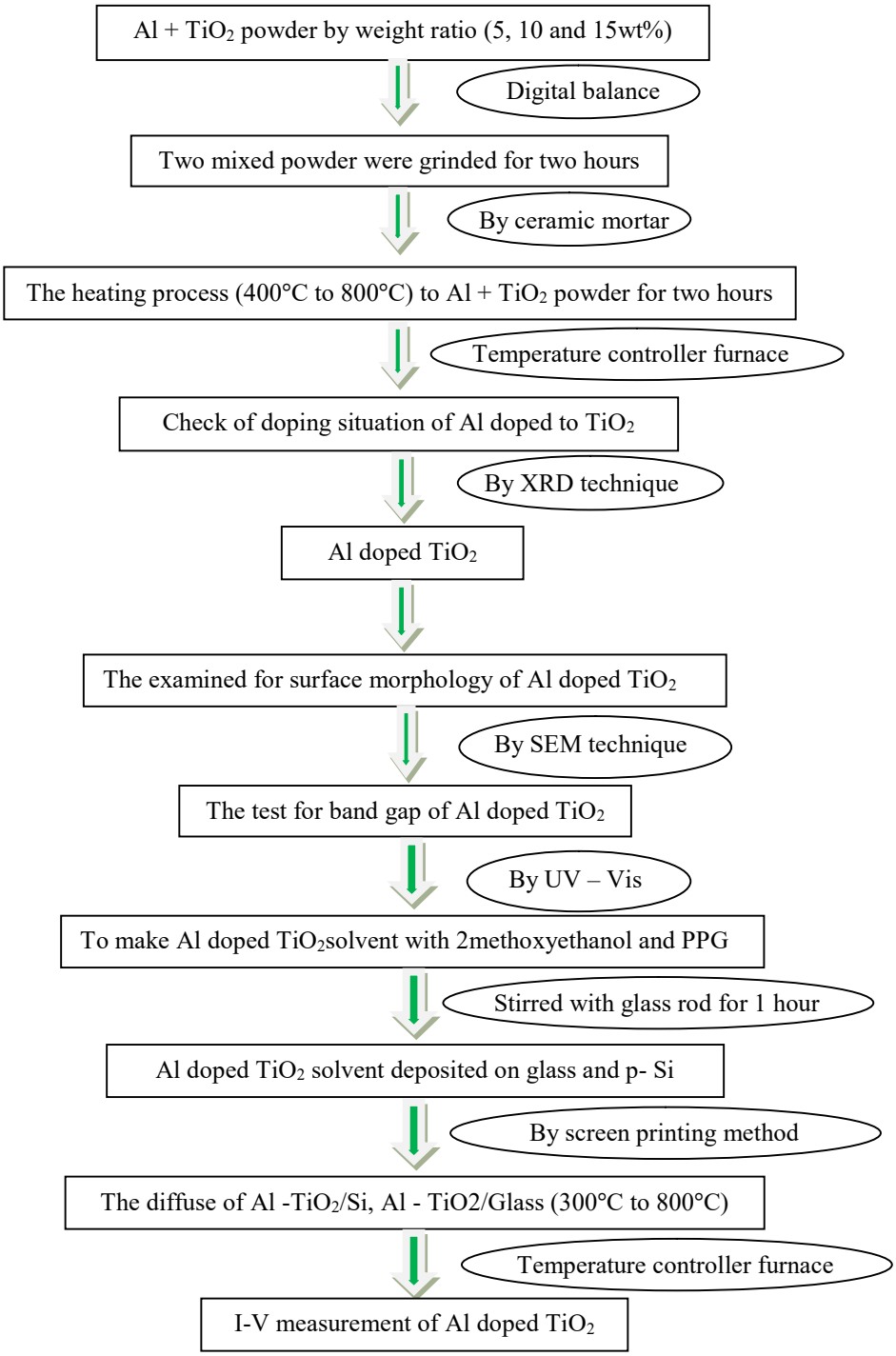


Figure 1. The sample preparation scheme of Al doped TiO_2 for thermal diffusion method

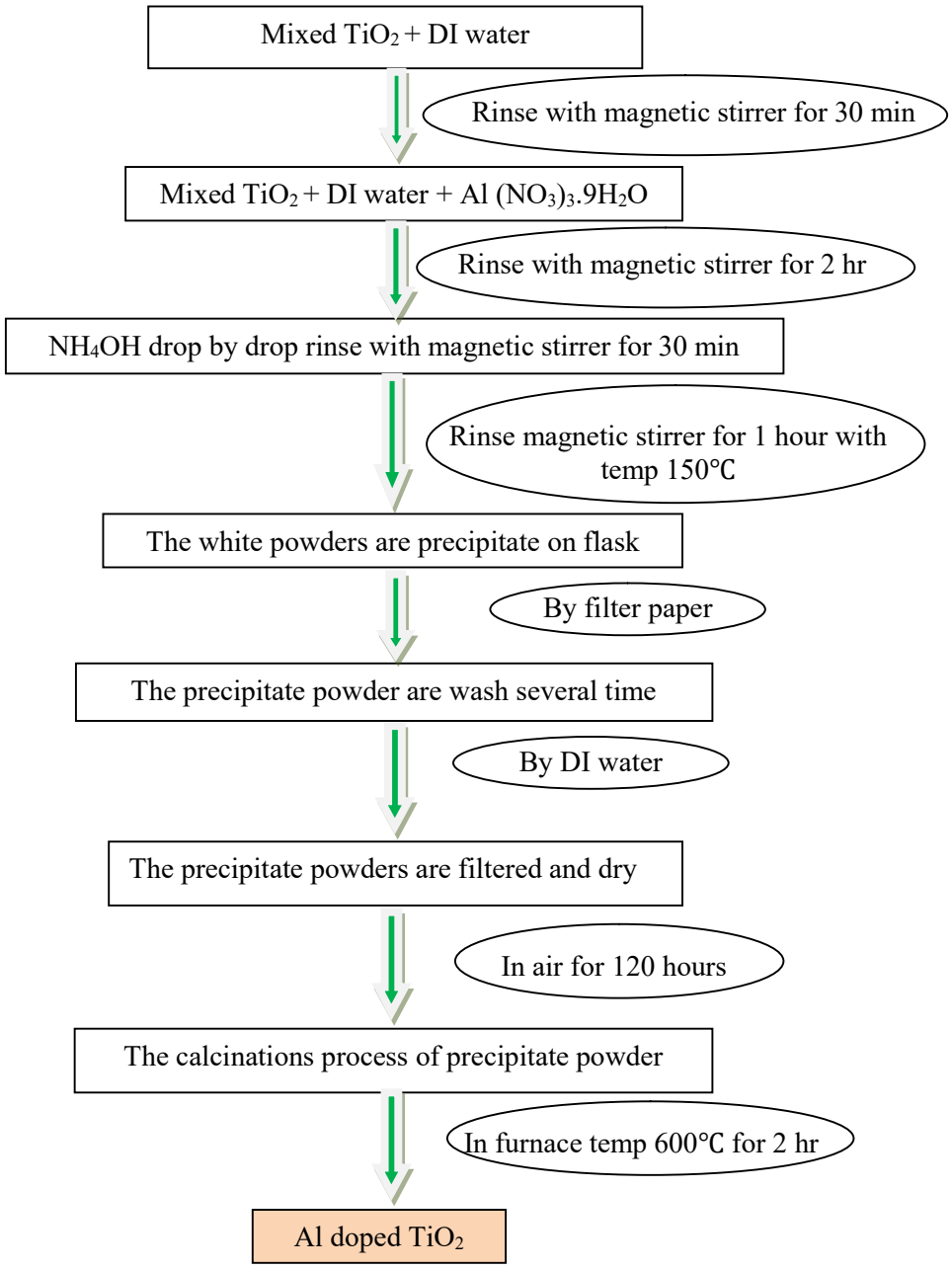


Figure 2. The sample preparation scheme of Al doped TiO_2 for co-precipitation method

Sample Preparation Photos

Figure 3. Weighing of chemicals with digital balance and grinding with aggregate mortar

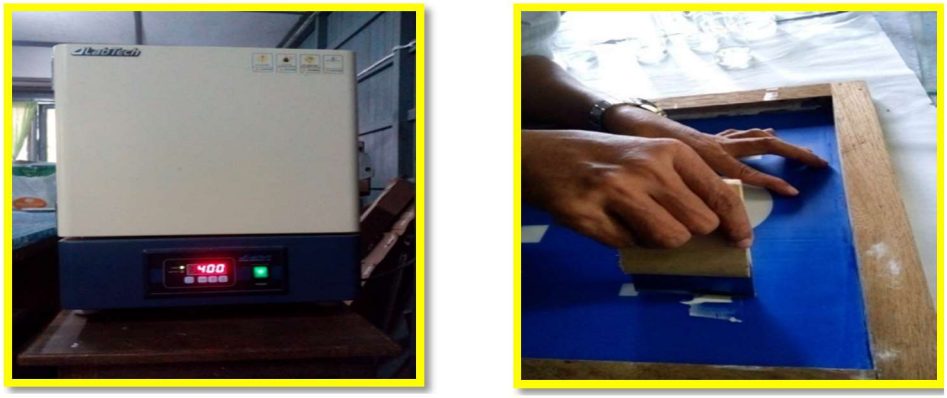


Figure 4. Heat treatment to mixed powder of Al and TiO2, Al doped TiO2 deposited on Si and glass by screen printing method

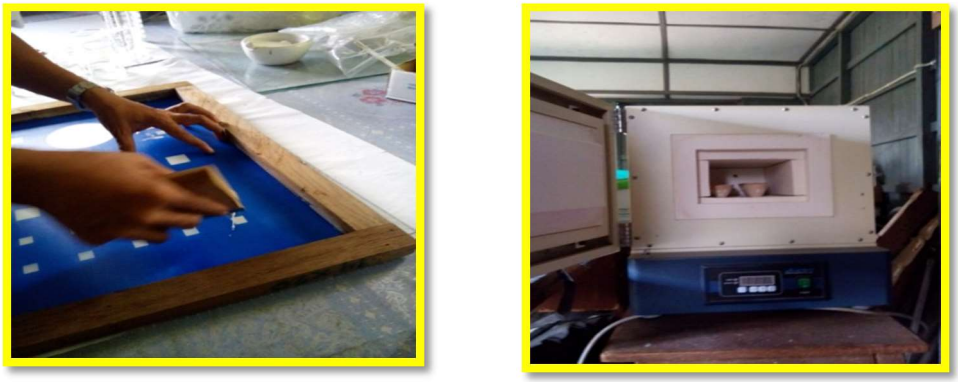


Figure 5. Sample deposition process by the screen printing method and heat treatment at different temperatures

Figure.6 Different doping ratio of Al doped into TiO_2 by co-precipitation method

Figure 7. Al doped TiO2 sample precipitate on flask, filter and dry in airfor120 hours

Experimental Data

The x-ray diffraction(XRD) analysis of Al doped TiO_2

The typical XRD patterns of pure TiO_2 and Al doped TiO2 were shown in Figure-8 to 11.Major peaks of Al doped TiO_2 is (101) can be attributed to tetragonal structure anatase form at doping temperature 400°C to 700°C. The diffraction major peaks of Al doped TiO2 at 800°C (15 wt%)are (110) and (101).The diffraction peaks of all samples were quite matching with the tetragonal TiO2 data [JCPDS card, No-71-1167 and 87-0920] but different form.In XRD pattern, (101) diffraction peak observed 2θ degree range between 25.055º to 25.335º for anatase form and rutile form 2θ degree is 27.225 º to 27.487 º. The variation of 2θ is depending on the Al doping concentration and2θ degree of Al doped TiO2 is smaller than pure TiO2 for anatase phase. In rutile phase, 2θ degree of Al doped TiO_2 is wider than pure TiO2. The 2θ degree is increase with decrease intensity of XRD peak for anatase form and reverse situation for rutile form. The XRD pattern intensity of TiO2 (101) peak is decrease with increasing Al doping ratio for anatase form and intensity peak increase with increasing doping ratio for rutile form.The lattice parameter “c” of Al doped TiO2 depicts as a function of Al doping concentration. The crystal structure of TiO2 is the same but change the anatase form to rutile form, it is depends on the doping temperature. As could

be seen, the lattice parameter "c" is 9.5204 Å for pure TiO2 and other "c" vales. With the increase in the Al concentration (5, 10 and 15 wt%), the lattice parameter "c" is differ from pure TiO2 and changes with randomly 9.5191 Å, 9.5279 Å and 5.4910 Å respectively for doping temperature 500°C.The increase in the lattice parameter "c" could be attributed to the Al atoms substitute in the Ti atoms in the lattice, and radius of the Al ion was smaller than that of the Ti ion.

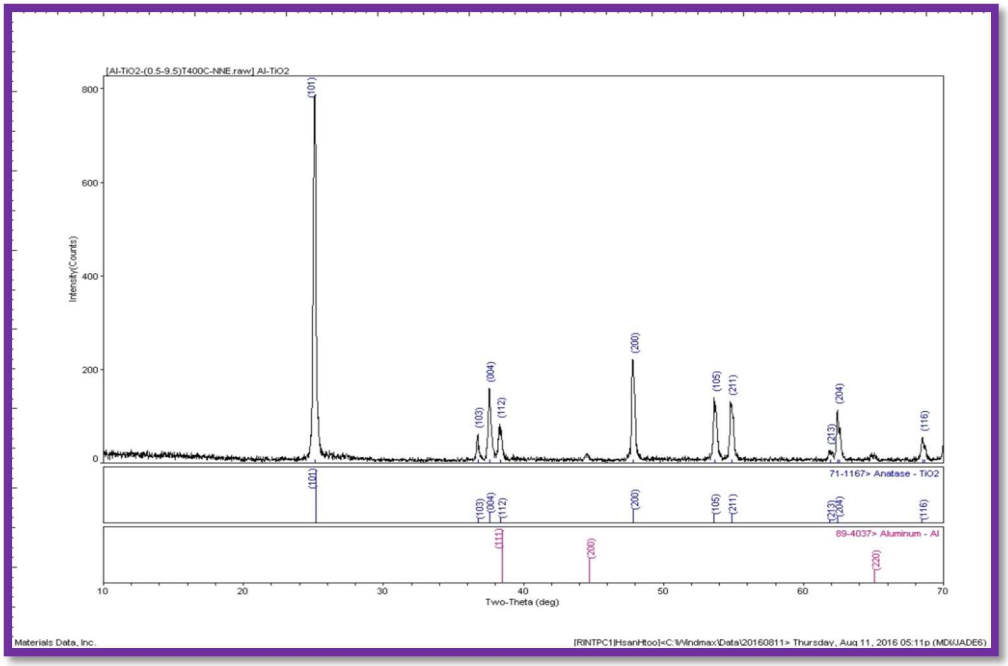


Figure 8. XRD analysis of Al doped TiO_2 (5wt% Temp 400°C)

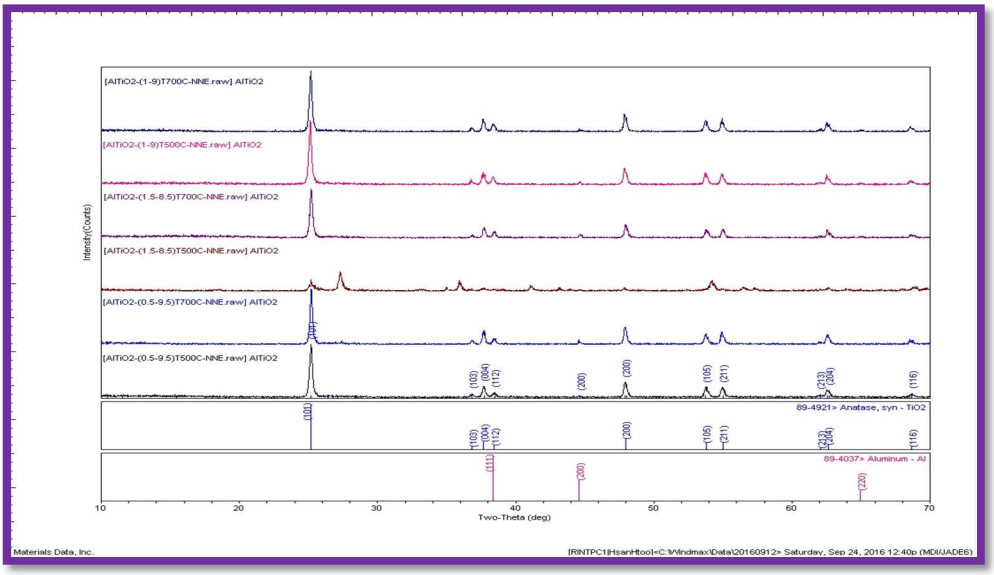


Figure 9. XRD analysis for comparison ofpureTiO2 and Al doped TiO2 at different doping ratios and temperatures

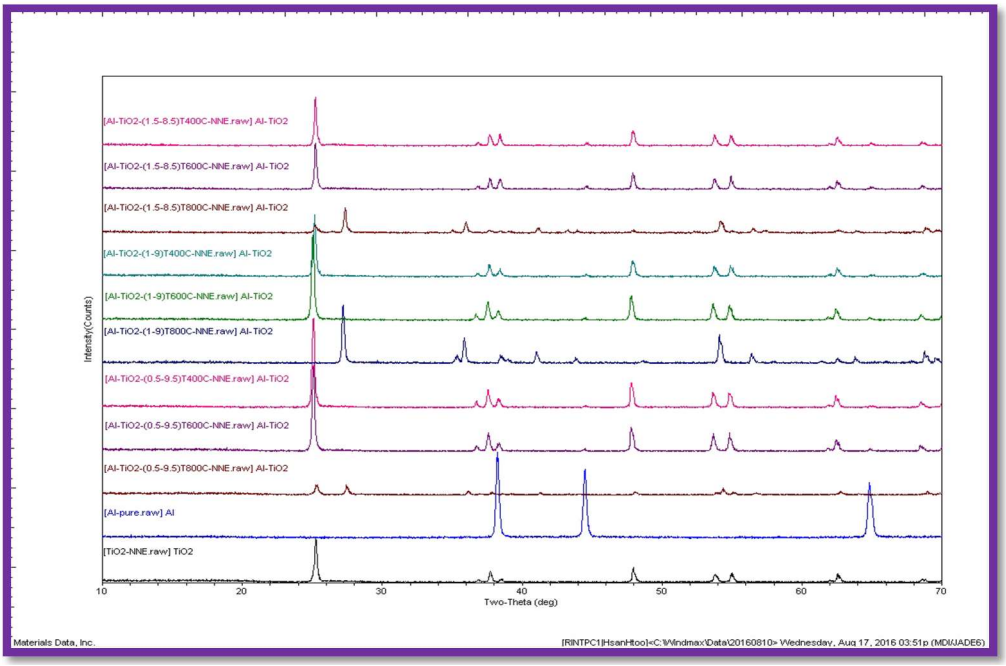


Figure 10. XRD analysis for comparison of Al doped TiO2 and pure TiO2 at different doping ratios and temperatures

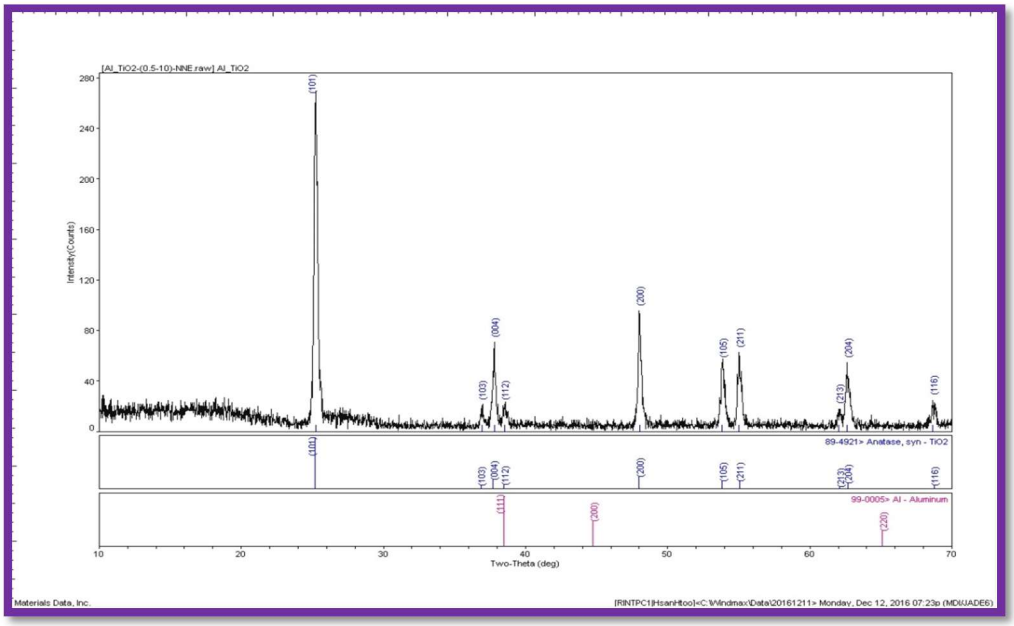


Figure 11. XRD analysis of Al doped TiO2 by co-precipitation method (5 wt%)

The scanning electron microscopy (SEM) analysis of Al doped TiO2

The surface morphology of the samples was investigated by scanning electron microscope (SEM) as shown in Figure-12. Al doped TiO2 (5wt%) particles appear several shape and grain size of these particles present in the size range between 30 nm- 60 nm. The surfaces morphology of Al doped TiO_2 powders for different doping temperatures are 400°C, 500°C, 600°C, 700°C and 800°C respectively. The SEM images are show generally uniform for doping temperatures 500°C, 600°C and 700°C not only doping temperature 400°C but also 800°C are different morphology forms. Doping temperature 500°C image is more uniform, sharp and clearly structure of other Al doped TiO_2images.

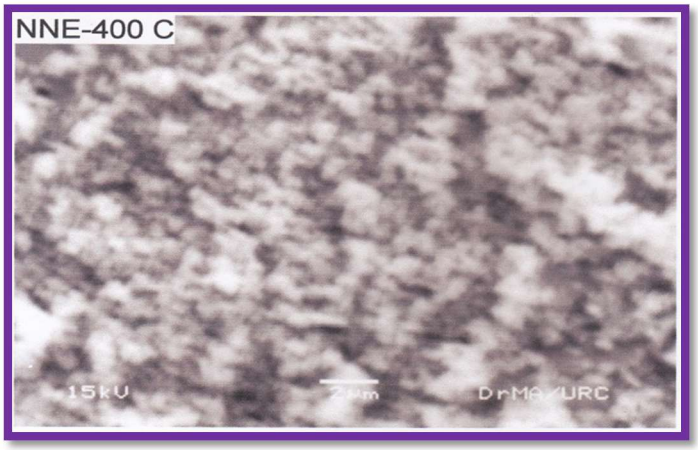


Figure.12 SEM analysis of Al doped TiO_2 (5wt%) at 400°C

The ultraviolet spectroscopy UV-Vis analysis of Al doped TiO2

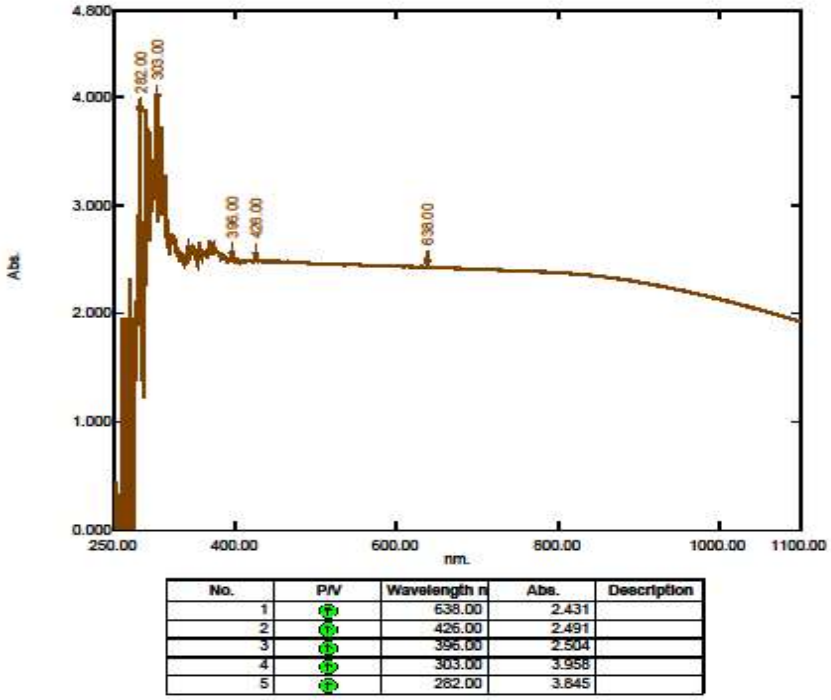
The measurement of the bandgap of materials is important in the semiconductor and solar industries**.** The term "bandgap" refers to the energy difference between the top of the valence band to the bottom of the conduction band. The electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition, the bandgap energy.

UV-Vis analysis of Al doped TiO2 particles are shown in Figure-13. The bandgap is vary with Al doping concentration for constant temperature 400° C as shown in fig 14. In this case, pure TiO2 has a bandgap 3.2 eV for anatase form as compared to bandgap of Al doped TiO2 are (1.944 eV, 2.431 eV, 1.525 eV, 1.395 eV, 1.893 eV) for doping ratio 5wt% at doping temperatures 400°C, 500°C, 600°C, 700°C and 800°C respectively. Al doping concentration is reduced the bandgap of pure TiO2. The bandgap of Al doped TiO2 is depending on different doping ratio in constant doping temperature 400°C as shown in Table-1. The bandgap of undoped TiO2 and Al doped TiO2 could be determined by finding the wavelength turning edge of the UV-Vis absorbance peak and equation as follow;

$$E_g = \frac{hc}{\lambda_{edge}}$$

Where, E_g = the bandgap energy h = Plank's constant

λ_{edge}= the wavelength of absorption edge c = the velocity of light



No.	P/V	Wavelength n	Abs.	Description
1		638.00	2.431	
2		426.00	2.491	
3		396.00	2.504	
4		303.00	3.958	
5		282.00	3.845	

Figure 13. UV analysis of Al doped TiO2 (5wt%) at 400°C

Table 1. UV analysis of Al doped TiO2 of different doping ratios and samedoping temperature

serial	Doping ratio (wt%)	Doping Temperature (℃)	Wavelength edge (nm)	Bandgap energy (eV)
1	5	400	638.00	1.944
2	10	400	412.00	3.009
3	15	400	378.00	3.280

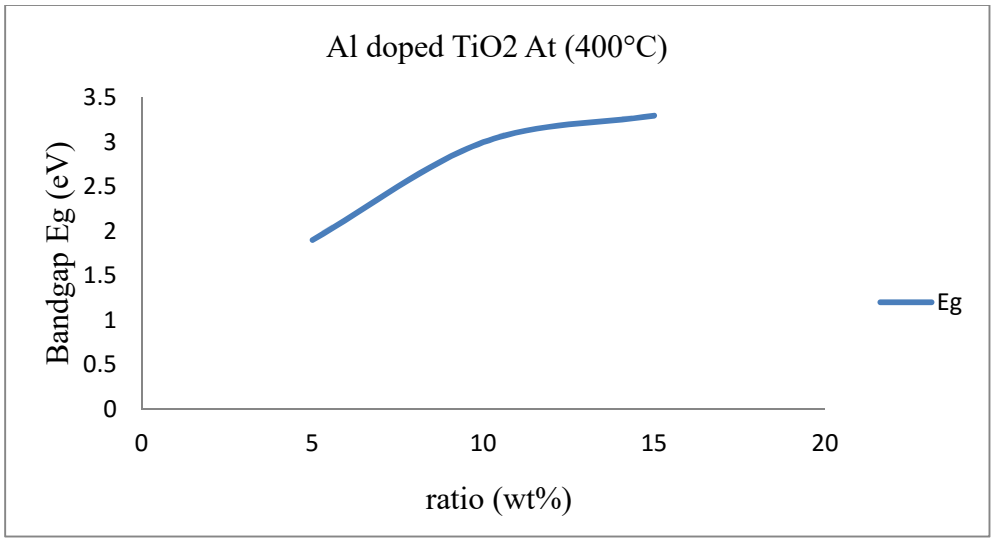


Figure 14. Bandgap energy of Al doped TiO_2

Current-Voltage Characteristics under Illumination Condition

Figure15 exhibits the photovoltaic behavior of the junction under the illumination condition. It is understood that the photoelectric effect is resulted from light induced electron-hole generation at the junction and particularly at the depletion region of the p-type silicon. The results of current-voltage (I-V) measurements for Al doped TiO2 deposited on Si films prepared at different diffusion temperatures. Photovoltaic properties of Al doped TiO2 deposited on Si films is depending on the different diffusion temperature and it is vary with light intensity. Photovoltaic of these films are increase with arise of light intensity. Al doped TiO2 deposited on Si films have been clearly exhibits sensitivity with light intensity.

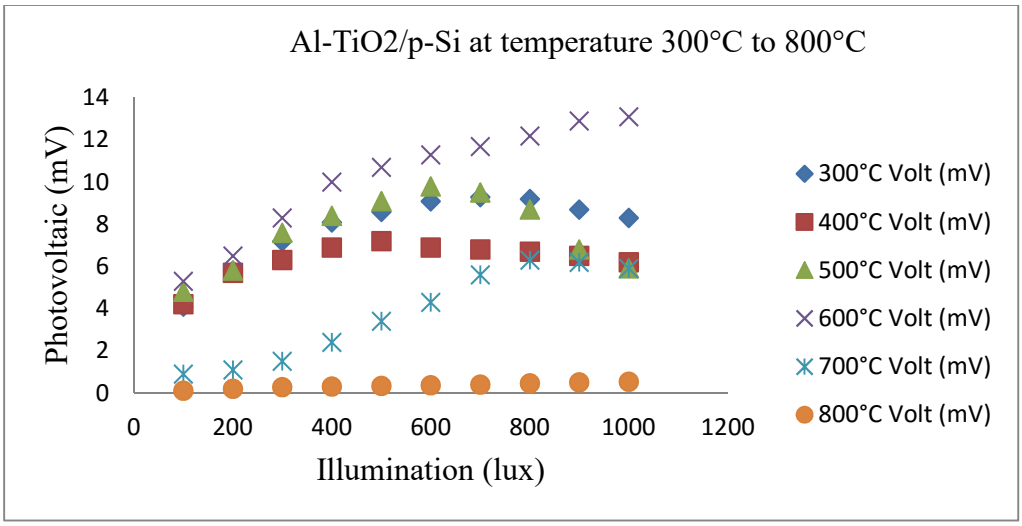


Figure 15. Photovoltaic measurement of Al doped TiO2 deposited on p-Si at 300°C to 800°C

Discussion

Alpowder doped into TiO2 powder with three different ratio of (5, 10 and 15 wt%) were used by thermal diffusion and co-precipitation methods. Al doping ratio 5wt% is thoroughly doped into TiO_2 and other Al doping ratios (10 and 15 wt%) are not completely doped into TiO_2 in thermal diffusion method and they are examined by the XRD and the results show Al is successfully doped into TiO2 in 5 wt% samples and other (10 and15 wt%) samples are not completely doped into TiO_2 in co-precipitation method. Al doped TiO2 is deposited on glass and p-type Si substrates by screen printing method. In this research screen printing method is use deposition process of Al doped TiO2 deposited on glass and Si. This method has some advantageous factors such as easy to do, homogeneous deposition and cheaper cost than other deposition techniques. According to the UV-Vis spectra with different doping ratio and temperature of Al doped TiO_2, the band gap energy of Al doped TiO_2 is varied with Al doping concentration. Moreover, it does not depend on doping temperature in same doping ratio.In doping temperature 800°C,XRD pattern of Al doping ratio 5wt% is tetragonal structure of anatase and rutile phase show simultaneously. In XRD pattern, Al doping ratio 10

wt% anatase peak (101) is gradually decrease than doping ratio 5 wt% rutile peak (110). XRD pattern of doping ratio 15 wt% is clearly show dominantly formed rutile phase only.

These two processes were successfully done with home-made equipment and hence cost cheaper price than other deposition techniques. And it is easily done in our laboratory. Al and TiO_2 are promising materials for optoelectronic devices and easy to buy in local market. Thermal diffusion method, co-precipitation method and screen printing method can be done in our laboratory.

Conclusion

Al doped TiO_2 sample of doping temperature 400ºC photo was clearer and sharper than other different doping temperature samples-photo has been seen by XRD. Al doped TiO2 particles were found to be of tetragonal structure, anatase phase of doping temperature 400ºC to700ºC. The doping temperature 800ºC is critical temperature for phase changes from anatase to rutile phase with same tetragonal crystal structure. Doping ratio (15 wt%) image shows highest intensity peak in co-precipitation method. The samples is clearly shows tetragonal particles with random form from SEM images. Comparing the two doping methods, these two samples have a little difference in XRD. The results of XRD pattern exhibit that thermal diffusion method has higher intensity peak than that result of co-precipitation method. According to the experimental results, thermal diffusion method is better than co-precipitation method for Al doped TiO_2 process. The angle of diffraction (2θ) is increased, varying with increasing doping concentration of Al at 400°C. The interplanar spacing "d" decrease with increasing Al doping concentration. According to the UV analysis pattern and calculation results, bandgap energy of Al doped TiO_2 is narrower than pure TiO_2 (3.2 eV, 3.0 eV) for anatase and rutile phase. The UV results of selected samples are 1.944 eV, 2.431 eV, 1.525 eV, 1.395 eV and 1.893 eV for 5wt% of Al doping temperatures 400°C, 500°C, 600°C, 700°C and 800°C respectively. Bandgap energy of Al doping ratio 10 wt% and 15wt% are 3.009 eV and 3.280 eV respectively. It is slightly different from pure TiO_2 at 400°C. In UV result, Al doped TiO_2 wavelength is between 378 nm to 889 nm and it indicates the inclusion within the range of

visible light and infrared region. Concentrative study on Al doped TiO_2 (5 wt%) ratio is best doping ratio for thermal diffusion method and (15 wt%) for co-precipitation method. I-V characteristic of diffusion temperature 600°C is optimum in this research. The photocurrent, voltage and resistance are varying with different diffusion temperature in constant illumination condition. The main advantages of the proposed synthesis are its simplicity and further work on the optimization of pure TiO_2 and Al doped TiO_2 tetragonal particles growth for electronic and optoelectronic applications in progress. Al doped TiO_2 can be used for gas sensor of NO_2 and CO gas.

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