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Fabrication of Al doped TiO_2 Nanopowder by Sol Gel Method for Gas Sensing and Solar Applications

Shubhra Mathur[1#], Rohit Jain[#]

[#]*Department of Physics, JaganNath Gupta Institute of Engineering & Technology, Sitapura Industrial Area, Tonk Road, Jaipur, Rajasthan, 302022, India*

Abstract*- Titanium dioxide nanopowder doped with aluminum (TiO_2/Al) is prepared by optimized sol-gel method. The specimens are annealed at 500^0C and 700^0C for 1 hour in air. X-ray diffraction pattern (XRD) exhibits pure anatase phase along with Al peaks in the case of TiO_2/Al specimen annealed at 500^0C whereas TiO_2/Al specimen annealed at 700^0C shows Al peaks with mixed (anatase/rutile) phase. The crystallite size of TiO_2/Al specimens annealed at 500^0C and 700^0C are 25±5 nm and 45± 5 nm respectively. The optical band gap of Al doped TiO_2 specimens are reduced to 2.60 eV for 500^0C and 2.37 eV for 700^0C as compared to their undoped TiO_2 specimens 3.0 eV and 2.75 eV respectively. Scanning electron microscopy (SEM) and Raman spectroscopy is used to understand the morphology and bonds present in TiO_2/Al specimens. Therefore doping of Al in TiO_2 reduces energy band gap value which increases its possible applications in the field of solar energy and gas sensing.

***Key words:* Titanium, Doping, Band gap, Sol-gel, Aluminium**

I. INTRODUCTION

Titanium dioxide (TiO_2) is a versatile material widely used in industry, research and environmental cleaning [1-3]. It exists in anatase, rutile and brookite phase. Anatase and brookite are metastable phases whereas rutile is the most stable phase. On heating anatase and brookite phase may transform to rutile phase. The structural differences of these phases also introduce difference in the gas sensing properties of titanium based devices [4]. Anatase phase of TiO_2 is n-type semiconductor which shows poor conductivity to be adopted for sensing oxidative gases [5]. Anatase to rutile phase transformation occurs at temperature above 600^0C. Recently it is reported that mixed (anatase/rutile) phase of TiO_2 exhibits superior gas sensing properties [6-7]. TiO_2 is also regarded as one of the capable candidate for solar energy application due to its optoelectronic and photochemical properties. The anatase structure is preferred for solar cell applications because of its potentially higher conduction band edge energy and lower recombination rate of electron- hole pairs. The photon absorption of semiconductors depends greatly on their band gap energy [8]. The energy band gap of anatase phase is 3.2 eV whereas for rutile phase it is 3.0 eV [9-10]. However most of the solar spectra remain unutilized because of TiO_2 large band gap [11].

It is important to focus on the improvement of the catalytic activities of TiO_2 through doping with different metal ion oxides such as Fe, Zn, Al, Cr, Ni etc. [12-16]. Doping of an element in TiO_2 can be done to achieve different results such as formation of new valence states in TiO_2, creation of charge carrier trapping sites, band gap reduction and surface area enhancement [3]. Khairy et al. studied the effect of metal doping in TiO_2 and reported that the doped TiO_2 nanoparticles in general show higher photocatalytic activities than the pure TiO_2 [17]. Kaur et al. observed that Ni doped TiO_2 sample shows better photocatalytic activity [18]. It was reported that doping of Fe in TiO_2 shows high sensitivity 86% towards H_2 gas [19]. Further doping of Al in TiO_2 may lead to improvement in the field of gas sensing and solar energy as it can be expected that Al ions go into the lattice as substitution metal dopant because ionic size of Al^{+3} and Ti^{+4} are very close to each other [20]. Therefore it will be beneficial to fabricate TiO_2 specimens with Al doping.

Sol gel is a versatile method used for the preparation of TiO_2 nanopowder. In our investigation we optimize the preparation method of TiO_2 nanopowder by using suitable concentration of starting material titanium isopropoxide (TTIP) [10]. The optimized preparation method leads to lower band gap of TiO_2 as compared to data reported in the literature [7, 10, 21, 22]. Hence we prepare TiO_2 specimens doped with Al by sol – gel method.

II. EXPERIMENTAL

Sol gel method is employed to prepare Al doped TiO_2 nanopowder specimens. Titanium isopropoxide (TTIP) and methanol are used as starting material. 0.5 g of Al metal powder is added into the mixture of 3.5 ml TTIP and 40 ml methanol already heated at 57±3^0C. The solution is stirred vigorously using magnetic stirrer. The gel is kept around 12 hours at room temperature for drying and thus the powder obtained is annealed at 500^0C and 700^0C in air for 1 hour [10]. Hence titanium dioxide doped with Al (TiO_2/Al) nanopowder is produced for further characterization.

III. RESULTS

X-ray diffraction pattern (XRD) of TiO_2/Al nanopowders annealed at 500^0C and 700^0C are recorded using CuK_α radiation as shown in Fig 1. It is observed that TiO_2/Al specimen annealed at 500^0C shows pure anatase phase with Al peaks. The TiO_2/Al specimen annealed at 700^0C depicts mixed (anatase/rutile) phase along with Al peaks. The crystallite size is calculated using Debye Scherrer’s formula

[1, 23-24] as 25±5 nm and 45±5 nm for TiO_2/Al specimens annealed at 500^0C and 700^0C respectively.

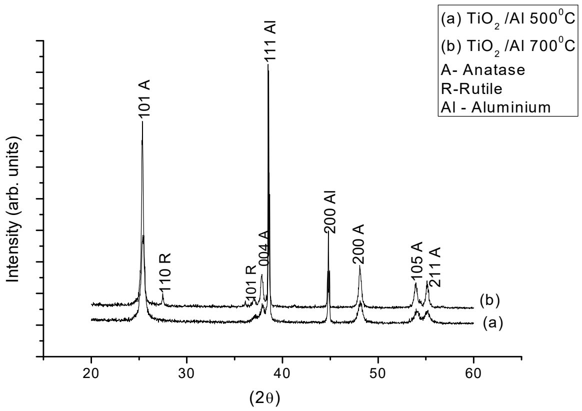

Fig. 1: X-ray diffraction pattern of TiO_2/Al specimens annealed at (a) 500^0C (b) 700^0C in air.

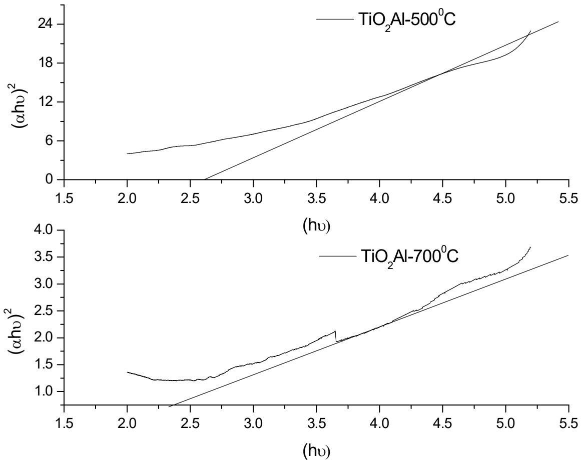

Fig. 2(a)

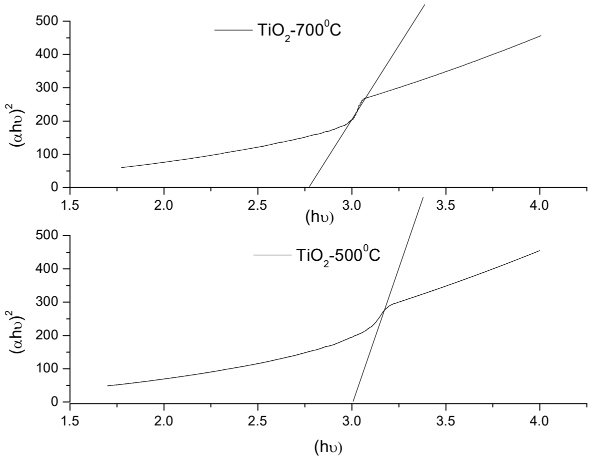

Fig.2(b)

Fig. 2: Tauc plots for TiO_2 (a) doped with Al (b) undoped specimens.

Fig. 2 (a) and Fig. 2 (b) shows Tauc plot obtained from UV spectra of TiO_2/Al and undoped TiO_2 specimens using Shimadzu-1800 instrument. The extrapolation of linear region at X-axis in Tauc plots yields energy band gap values as 2.60 eV and 2.37 eV for TiO_2/Al specimens annealed at 500^0C and 700^0C [1, 25].

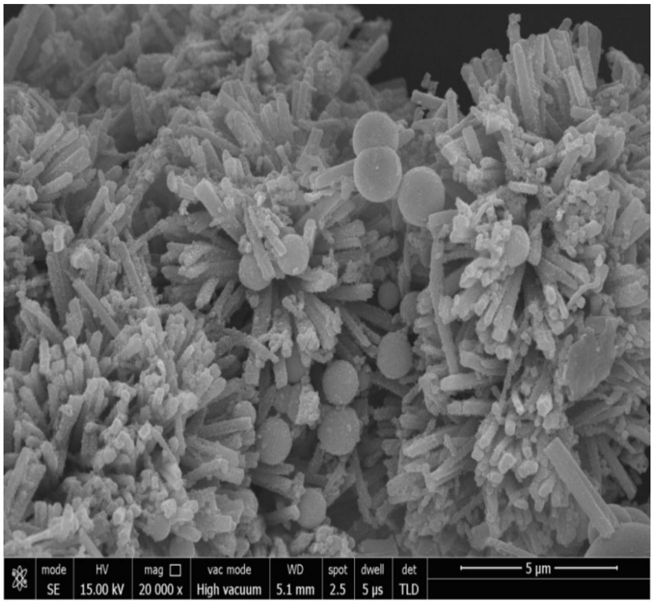

Fig. 3(a)

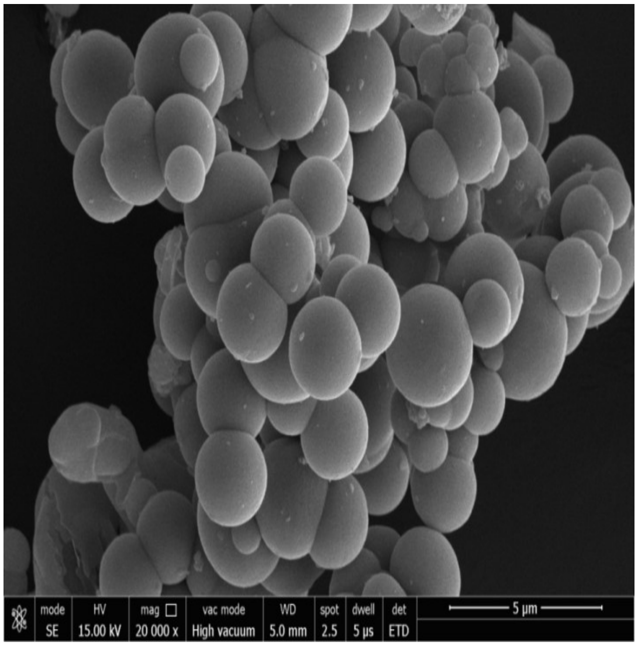

Fig.3(b)

Fig. 3: SEM images of (a) TiO_2-Al annealed at 500^0C and (b) TiO_2-Al annealed at 700^0C.

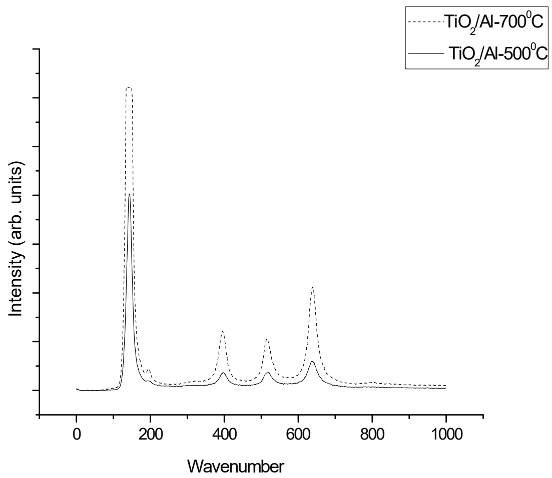

Fig.4: Raman spectra of TiO_2/Al specimens annealed at 500^{0}C and 700^{0}C.

Scanning electron microscopy is used to examine surface morphology of TiO_2/Al specimens as shown in Fig. 3 (a) and Fig. 3 (b). It is observed that TiO_2/Al specimen annealed at 500^{0}C exhibits mostly cylindrical shaped morphology whereas TiO_2/Al specimen annealed at 700^{0}C depicts particles in spherical shape [26-27]. Raman spectra of TiO_2/Al nanopowder as shown in Fig. 4 exhibit bands located at 144 cm^{-1}, 399 cm^{-1}, 515 cm^{-1} and 641 cm^{-1} corresponding to anatase phase of TiO_2 [28].

IV. DISCUSSION

The presence of Al peaks with anatase and mixed (anatase/rutile) phase confirms the doping of Al in TiO_2 as suggested by X-ray diffraction pattern. The crystallite size of TiO_2/Al nanopowder specimens increases with increase in annealing temperature. The energy band gap values obtained from Tauc plots for TiO_2/Al specimens are lower (2.60 eV for 500^{0}C and 2.37 eV for 700^{0}C) as compared to their undoped TiO_2 specimens (3.0 eV for 500^{0}C and 2.75 eV for 700^{0}C) as well as data reported in the literature [10, 11, 29]. This shows that doping of Al in suitable amount may create energy levels in the band gap of pure TiO_2 above its valence band which causes reduction in energy band gap. Hence a spectral shift from UV region to visible region occurs due to doping of Al in TiO_2 [3]. It is noteworthy here that the energy band gap value decreases with increase in crystallite size [29].

Nemade et al. reported that TiO_2 specimen doped with Al exhibits sensitivity towards LPG [28]. The presence of mixed (anatase/rutile) phase shows higher sensitivity towards H_2 gas as suggested by Enachi et al. [6]. Choi et al. shows that Al doped TiO_2 gas sensors were found to be more selective and sensitive to CO and O_2 at an operating temperature of 600^{0}C than pure TiO_2 powders [30]. TiO_2 doped with Al also show sensitivity to H_2S gas at 200^{0}C with fast response and recovery time [31]. It is also reported that doping of Al in TiO_2 increases efficiency of solar cells [3]. Huang et al. reported that a low doping concentration of 0.5 wt% Al in TiO_2 increases photo voltage and fill factor which enhances DSC performance with an overall conversion efficiency of 5.8 % higher than the non-doped specimen [32-33]. In light of the data reported in literature as prepared TiO_2/Al specimens may show interesting behaviour in solar energy and gas sensing applications due to its reduced energy band gap value and existence of mixed (anatase/rutile) phase.

V. CONCLUSIONS

1. The doping of Al in TiO_2 reduces energy band gap value which enhances its application in solar energy and gas sensing.
2. X-ray diffraction (XRD) pattern of TiO_2/Al specimen annealed at 500^{0}C exhibits pure anatase phase with Al peaks whereas TiO_2/Al specimen annealed at 700^{0}C shows mixed (anatase/rutile) phase along with Al peaks and there crystallite size increases with increase in annealing temperature.

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