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SYNTHESIS AND CHARACTERIZATION OF TIO_2/PS NANO STRUCTURE FOR SENSOR APPLICATIONS

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***Abstract*— Nanocrystalline *n*-typeTiO_2 thin film is coated on high porosity porous silicon (PS) by sol-gel spin coating method. TiO_2 was infiltrated into the pores of PS and thereby making active layer. X-ray diffraction (XRD), Scanning electron microscopy (SEM), Photoluminescence (PL) and Fourier transform infrared spectroscopy (FTIR) studies have been carried out to examine the characteristics of TiO_2/PS structure. XRD results confirm the formation of high quality TiO_2 tetragonal structure on PS surface and along with PS peak, anatase & rutile peaks of TiO_2 were also observed. The grain sizes calculated for TiO_2 thin film, Porous Silicon and TiO_2/PS are 85 nm, 32 nm and 25 nm respectively. SEM images reveal that the pores are filled by TiO_2 showing island like structures. Blue and Green PL emission peaks were observed at an excitation of 410 nm in PL spectrum. The presence of Ti-O-Ti, Si-O-Si & Si-O-Ti bands were observed from FTIR study. From the results it is observed that the described structure can be used for sensor applications.**

Keywords- TiO_2 thin film; Porous Silicon; Sol-gel method; XRD; SEM; PL and FTIR.

I. INTRODUCTION

The discovery of intense photoluminescence (PL) at room temperature in the visible spectral region from porous silicon (PS) has resulted in a great deal of research for silicon based optoelectronic devices [1]. In recent years, much effort has been focused on the elaboration of heterojunctions based on PS due to its potential applications in optoelectronics devices**.** The metal oxide semiconductors have received significant attention of the researchers owing to their potential applications. In recent years, Titanium dioxide (TiO_2) has become an interesting metal oxide material because of its inimitable properties like transparency, chemical stability, high refractive index (η=2.40) and high dielectric constant. The direct energy band gap of TiO_2 is 3.02 eV – 3.23 eV [2]. TiO_2 coated on porous silicon is applied in the field of photovoltaic and photoelectrochemical cells [3]. Different methods have been proposed to deposit TiO_2 films on PS layers, such as Sputtering [4], Pulsed laser deposition (PLD) [5], Chemical vapour deposition (CVD) and sol-gel techniques [6, 7]. The sol-gel method has an advantage of easy control of chemical composition of thin layers. In this work, TiO_2 films were deposited on PS substrates by sol-gel spin coating technique which is a simple, flexible and low cost method. The structural, surface morphological and optical properties of TiO_2/PS heterojunction have been studied in detail.

II. EXPERIMENTAL DETAILS

Porous Silicon was formed by using electrochemical anodization of *p*-type (1 0 0) Si wafer having a resistivity of 0-100 ohm cm. Anodization was carried out in 12.5 % of HF concentration in the electrolytic solution for 10 minute at 50 mA/cm^2 current density. The electrochemical etching was done in a single tank Teflon anodizing system. In this system the anode is *p*-Si wafer and the cathode is platinum rod [8].

TiO_2 sol was prepared using titanium tetra isopropoxide (TTIP), ethanol (as solvent) and acetylacetone. 1 ml of TTIP was mixed with 10 ml of ethanol and stirred for 10 minute using magnetic stirrer to obtain a milky white solution. In this mixture 1 ml of acetylacetone was added and stirred for 30 minute. An orange coloured solution was obtained. Again 10 ml of ethanol was added to the solution and stirred vigorously for 3 hours. The prepared sol was kept in an open air for 48 hours for aging and the gel is formed.

TiO_2 film was deposited on the PS substrate by using the sol-gel spin coating method. To coat the TiO_2 film, the gel was dropped onto the PS substrate, and rotated at a speed of 3000 rpm for 10s by using the spin coater. The substrate was then dried at 150˚C for 10 minutes in a Muffle furnace. The process of spinning and drying was repeated for seven more times to obtain 8 coatings. Finally the coated film was post annealed at 550˚C for 1 hour.

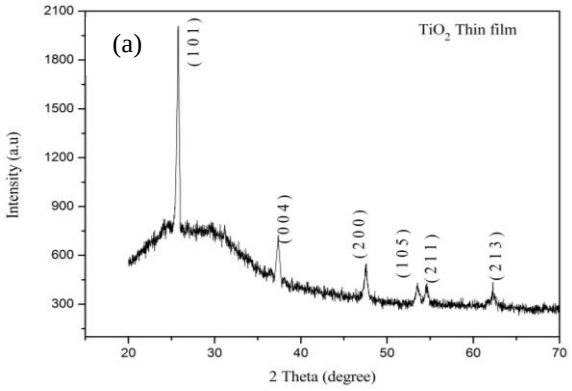
The X-ray diffraction (XRD) spectrum was recorded using Bruker D8 advanced X-ray diffractometer using Cu $K\alpha_1$ (1.54060 Å) source. The surface morphology observation was done by Quanta SEG - 200 FESEM. The photoluminescence excitation spectra of the samples were obtained with a Shimadzu RF 5301 spectrophotometer. A pulsed Xenon lamp

was built in the spectrometer as the excitation source. Shimadzu 8400 s FTIR spectrometer having a wave number range of 3000 – 400 cm^{-1} has been used to identify the species and bonding on the surface of the samples. All measurements were carried out at room temperature.

III. RESULTS AND DISCUSSIONS

A. XRD analysis

Figure 1 (a-c) shows the XRD patterns of TiO_2 thin film, PS and TiO_2/PS respectively. XRD pattern (Figure 1.c) of TiO_2/PS structure exhibits a dominant peak at 2θ= 68.89º corresponding to the reflections from (4 0 0) plane (JCPDS File No. 89-2955) and is due to crystalline Si substrates. Another trivial peak, which occurs at 69.07º, is due to the porous layer. Other diffraction peaks of (1 0 1), (1 1 0), (1 1 2), (2 0 0) and (1 0 5) orientations of TiO_2 thin film corresponding to anatase phase and (2 1 1) orientation, which corresponds to rutile phase of TiO_2 thin film, with tetragonal structure were also observed.



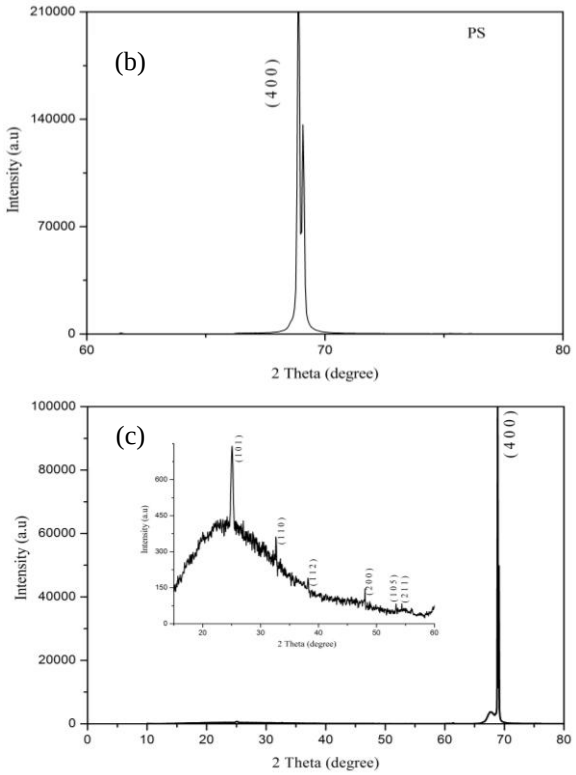


Figure 1(a-c) XRD patterns of TiO_2 thin film, PS and TiO_2/PS

The crystallite size was determined using a well-known Debye- Scherrer's formula,

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

where k= 0.94, λ= 1.5406Å, β= Full Width Half Maximum (FWHM) and θ= Diffracting angle.

The calculated crystallite sizes are 85 nm, 32 nm and 25 nm for TiO_2 thin film, porous silicon and TiO_2/PS respectively. These results imply that the TiO_2 thin film grown on PS exhibit better crystallinity and the reason for the decrease in crystalline size in TiO_2/PS may be due to TiO_2 nanoparticles that infiltrated into the pores would have established good nucleation sites.

B. SEM analysis

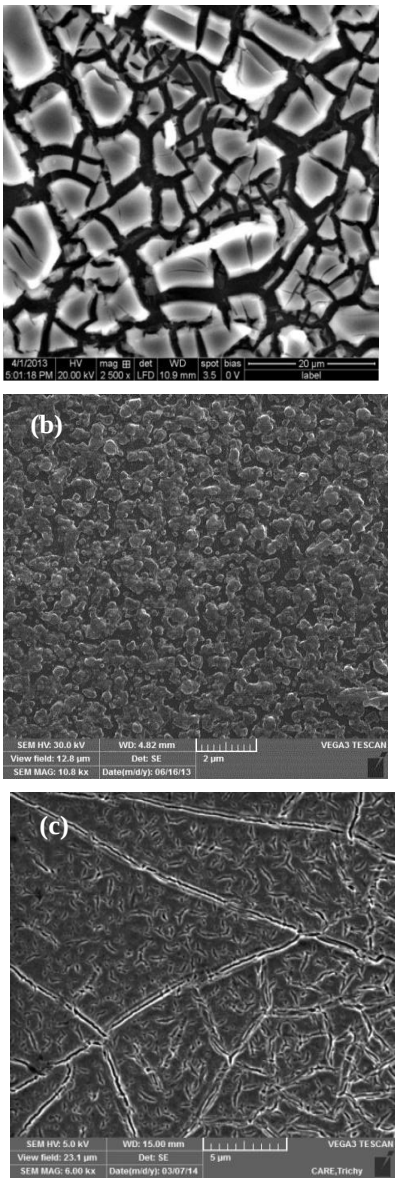


Figure 2(a-c) SEM images of TiO_2 thin film, PS and TiO_2/PS

Figure 2 (a-c) shows the plane-view SEM images of TiO_2 thin film, PS and TiO_2 thin film grown on PS respectively. TiO_2 thin film coated on glass substrate shows the homogeneous island with cracks in Figure 2(a). The SEM image of PS in Figure 2(b) shows a large number of homogeneous pores and voids. Figure 2(c) shows TiO_2 coated on PS substrate and the image shows partial filling of the TiO_2 particles into the pores of PS.

C. Photoluminescence analysis

Figure 3(a), (b) and (c) show photoluminescence spectra of TiO_2 thin film, PS and TiO_2/PS excited at 410 nm.

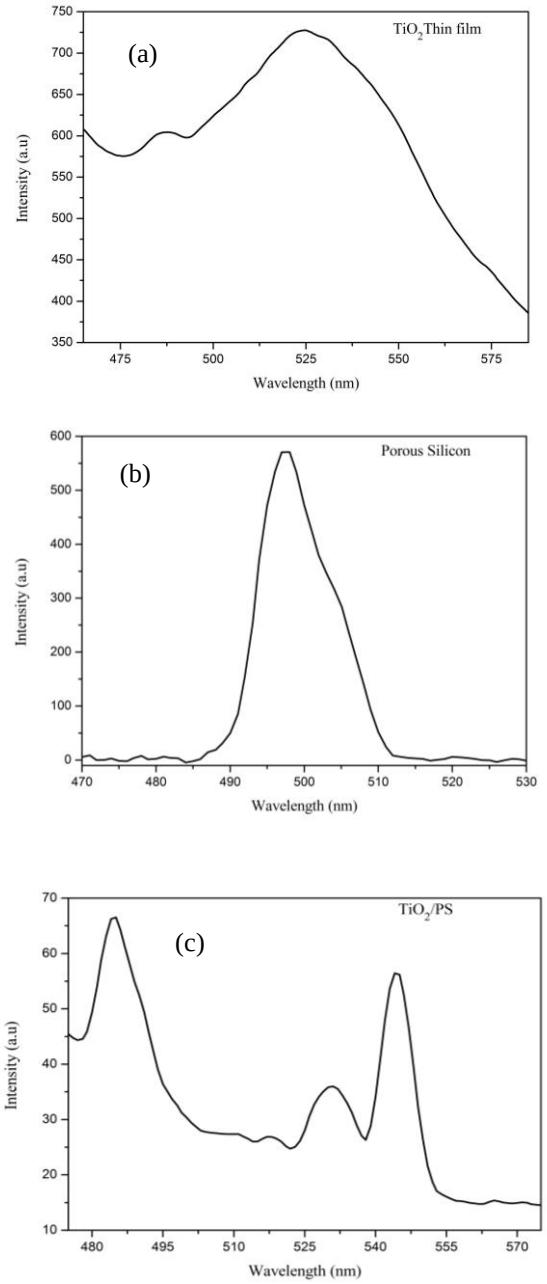


Figure 3(a-c) PL spectra of TiO_2 thin film, PS and TiO_2/PS

The presence of three strong emission peaks at 485 nm, 530 nm, 545 nm and a shoulder peak at 518 nm were identified in TiO_2/PS in Figure 3(c). The peaks at 485 nm and 530 nm are the same as the peaks present in the PL spectrum of TiO_2 thin film (Figure 3(a)). The emission peak at 485 nm is attributed to impurities and defects and the peak at 530 nm is due to oxygen vacancies [9]. The occurrence of broad emission peak at 545 nm may be attributed to transition among the quantum confined states in nanoscale Si, which are influenced by the surface bonds.

D. FTIR analysis

Figure 4 shows the FTIR transmission spectrum of TiO_2 thin films coated on porous silicon. From the Figure 4 it was observed that TiO_2/PS sample exhibits bands at 430 cm^{-1}, 560 cm^{-1}, 817 cm^{-1}, 930 cm^{-1}, 1080 cm^{-1}, 2300 cm^{-1}. The FTIR bonds and their vibration modes are listed in Table.1.

The transmission bands at 430 cm^{-1} and 560 cm^{-1} corresponds to Ti-O-Ti stretching vibration modes of anatase phase. The bands at around 820 cm^{-1} and 1080 cm^{-1} were attributed to Si-O-Si of symmetric and asymmetric stretching modes of vibration. The peaks observed in the region 2000-2200 cm^{-1} are assigned to Si-H_x (x=1, 2, 3 … n) bonds. The strongest peak at 2300 cm^{-1} corresponds to O_3SiH stretching mode.

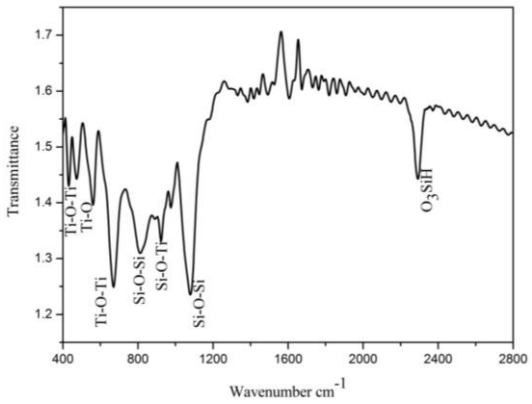


Figure 4 FTIR spectrum of TiO_2/PS

TABLE 1 FTIR Bonds & Vibration modes of TiO_2 thin film on PS substrate

Wavenumber cm^{-1}	Bonds	Vibration mode	Reference
435	Ti-O-Ti	Stretching	[10]
560	Ti-O	Stretching	[11]
817	Si-O-Si	symmetric stretching	[12]
930	Si-O-Ti	stretching	[13]
1080	Si-O-Si	asymmetric stretching	[8]
2000 -2200	Si-H_x(x=1,2,3…n)	Stretching	[14]
2300	O_3SiH	Stretching	[15]

IV. Conclusion

TiO_2 thin film onto porous silicon substrate was successfully coated by sol-gel spin coating method. The structural, surface morphological and optical properties were investigated. XRD result showed that the most dominant peak with (4 0 0) reflection corresponds to silicon and the other diffraction peaks of TiO_2 thin film having anatase and rutile phase were also present. Surface morphology of TiO_2/PS shows that the pores are filled by TiO_2 particles. Strong emission peaks at 485 nm, 530 nm and 545 nm are observed in photoluminescence spectrum of TiO_2/PS structure. The presence of Si-O-Ti band in FTIR study confirms the incorporation of TiO_2 in Si. These results enable us to conclude that the heterojunction structure may be used for sensor application.

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