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Characterization studies of tin oxide/porous silicon heterojunction in view of optoelectronics application

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Abstract: Tin oxide (SnO₂) and porous silicon (PS) are two types of materials that have been extensively investigated for optoelectronic applications. In this work, properties of SnO₂ thin film layer deposited on PS by sol-gel spin coating have been investigated. SnO₂ was incorporated into the pores of PS and thereby making a protecting layer. XRD result suggests the formation of a good crystalline quality SnO₂ tetragonal structure on PS surface and peaks pertaining to PS along with those corresponding to SnO₂ were observed. SEM images confirm the pore filling and surface coverage. The covalently grafted inorganic molecules on silicon surfaces are confirmed by transmission FTIR spectra. An enhancement of PL emission has been observed after SnO₂ film deposition on PS. From the results, the technique described herein is a cost effective method for producing photoluminescence enhanced SnO₂/PS structure that can be used for optoelectronic application.

Keywords - SnO₂ thin film; Porous Silicon; Sol-gel method; XRD; SEM; FTIR and PL.

Introduction and Experimental:

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. In recent years, much effort has been focused on the elaboration of heterojunctions based on PS due to its potential applications in the silicon-based optoelectronics devices. The metal oxide semiconductors have received significant attention of the researchers owing to their potential applications. Tin dioxide (SnO₂), a wide band gap ($E_g = 3.6$ eV) n-type semiconductor. During the last few years, SnO₂ has been investigated as an advanced material for electronic and optoelectronic devices. Obviously investigations should be performed on SnO₂/PS heterojunctions. In this work, SnO₂ films were deposited on PS substrates by sol-gel spin coating technique which is a simple, flexible and low cost method. The physical properties of SnO₂/PS heterojunctions had been studied in detail.

PS layers were formed by using electrochemical anodization of p-type (1 0 0) Si wafers with a resistivity of 0-100 ohm cm. Anodization was carried out in a 1:1 ratio of HF and ethanol solution for 10 minute at 50 mA/cm² current density. SnO₂ films were deposited on the PS substrates by using the sol-gel spin coating method. The required precursor solution was prepared by dissolving 8.37 g SnCl₂·2H₂O in 100 ml of ethanol. This sol-gel was spin-coated on the PS substrates at 3000 rpm for 30 s at room temperature. To evaporate the solvent, the coatings were then dried in a furnace at 100°C for 10 minutes. By repeating the process to coat 10

times onto PS substrates, SnO_2/PS structure was obtained. Finally the sample was annealed in furnace at 500°C for 1 h.

Results and Discussion:

XRD and SEM analysis

XRD analysis provides most definitive structural information and Figure 1 (a-c) shows the XRD patterns of the SnO_2 thin films, PS and SnO_2/PS samples respectively. XRD pattern shows that the SnO_2/PS structure (Figure 1 c) exhibit a dominant diffraction peak at $2\theta = 68.9^\circ$ corresponding to the PS (4 0 0) layer along with SnO_2 diffraction peaks of (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (0 0 2) and (3 1 0) orientations are also observed. These results imply that the SnO_2 thin films grown on PS exhibit better crystallinity. The crystallite size was calculated using Debye–Scherrer formula. The size of the crystallites of the SnO_2 films obtained from XRD were 28 nm, 18 nm and 15 nm for SnO_2 film, PS layer and SnO_2/PS respectively. The decrease in crystallite size indicated that the SnO_2 nano-particles that have infiltrated into the pores established good nucleation, which would induce the SnO_2 nano-particles to grow along the preferred orientation. From the XRD results, it can be seen that the PS substrate can serve as a good template during SnO_2 growth. These observations are in good agreement with the reported results [1].

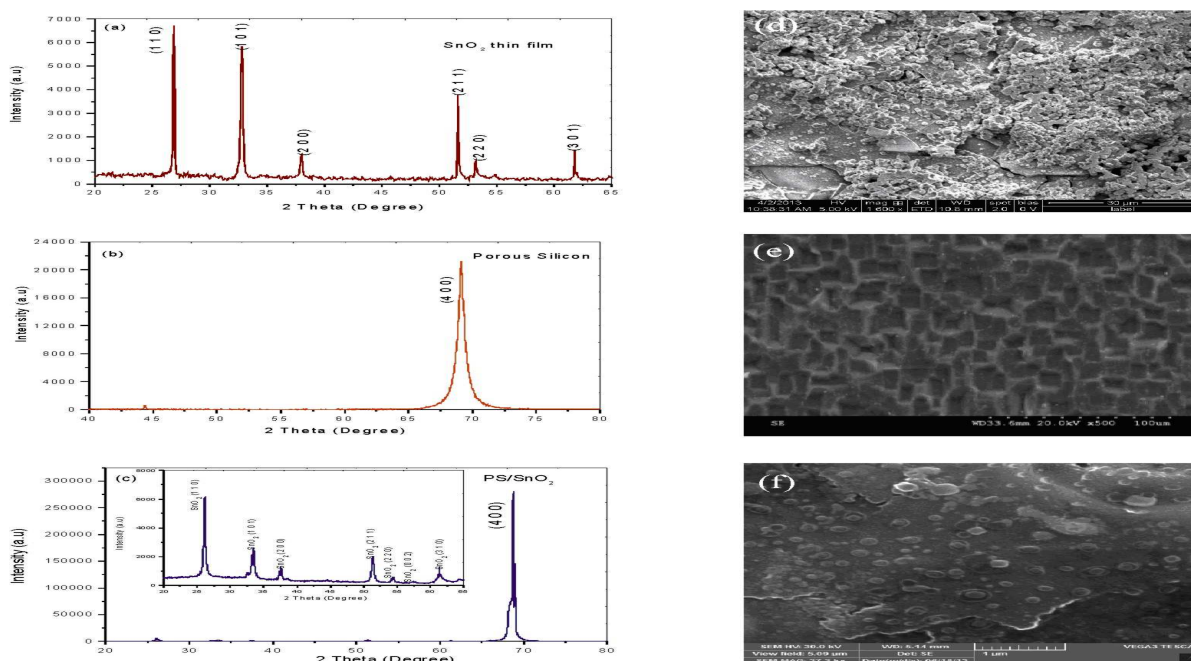


Figure 1 (a-c) XRD pattern and (d-f) SEM images of SnO_2 tin film, PS and SnO_2 / PS

Figure 1 (d-f) shows plane-view SEM images of the SnO_2 thin film, PS and SnO_2 thin film grown on PS respectively. Figure 1(d) shows SEM image of SnO_2 thin film deposited on glass substrate and the morphology shows all the particles are almost spherical in shape. Figure 1 (e) shows that the surface of the PS layer was a sponge-like structure which consists of large number of ‘pores’ and ‘voids’. These ‘pores’ and ‘voids’ make porous silicon an adhesive surface for accommodating SnO_2 into its pores. From the SEM image (Figure 1(f)), it was obvious that the SnO_2 thin film was closely connected with the PS substrate. Thus, the SnO_2 thin film acted as a transparent capping and providing a good coverage of the crystallite surface on the PS substrate, which could improve the structural stability of the PS substrate. The surface roughness is also increased and it is attributed to the partial filling and formation of SnO_2 nanoparticles in the pores of PS.

PL and FTIR analysis

PL spectra observed for SnO_2 thin film (a), PS (b) and SnO_2/PS heterojunction (c) were indicated in Figure 2. The PL spectrum of SnO_2 film show two emission peaks at 422 nm and 487 nm, which may be assigned to native defects such as oxygen vacancies or tin interstitials. The PL spectrum of the PS layer (Figure 2 b) exhibits a broad peak at 606 nm (red region), suggesting that hydride related luminescence process is active in PS [2]. The occurrence of strong PL spectra may be attributed to the transition among the quantum confined

states in nanoscale Si, which are influenced by the surface bonds. The PL spectra of SnO₂/PS heterojunction shows a broad peak at 685 nm (Figure 2 c) and the peak shift to a higher wavelength of 685 nm (*i.e.*, red shift) suggest modification at the SnO₂/PS interface. This may be due to the incorporation of SnO₂ particles into the pores and the red shift may be due to the shape and size of PS coated with SnO₂ film. This is also confirmed by the XRD and SEM results. An enhancement of PL emission has been observed after SnO₂ film deposition on PS.

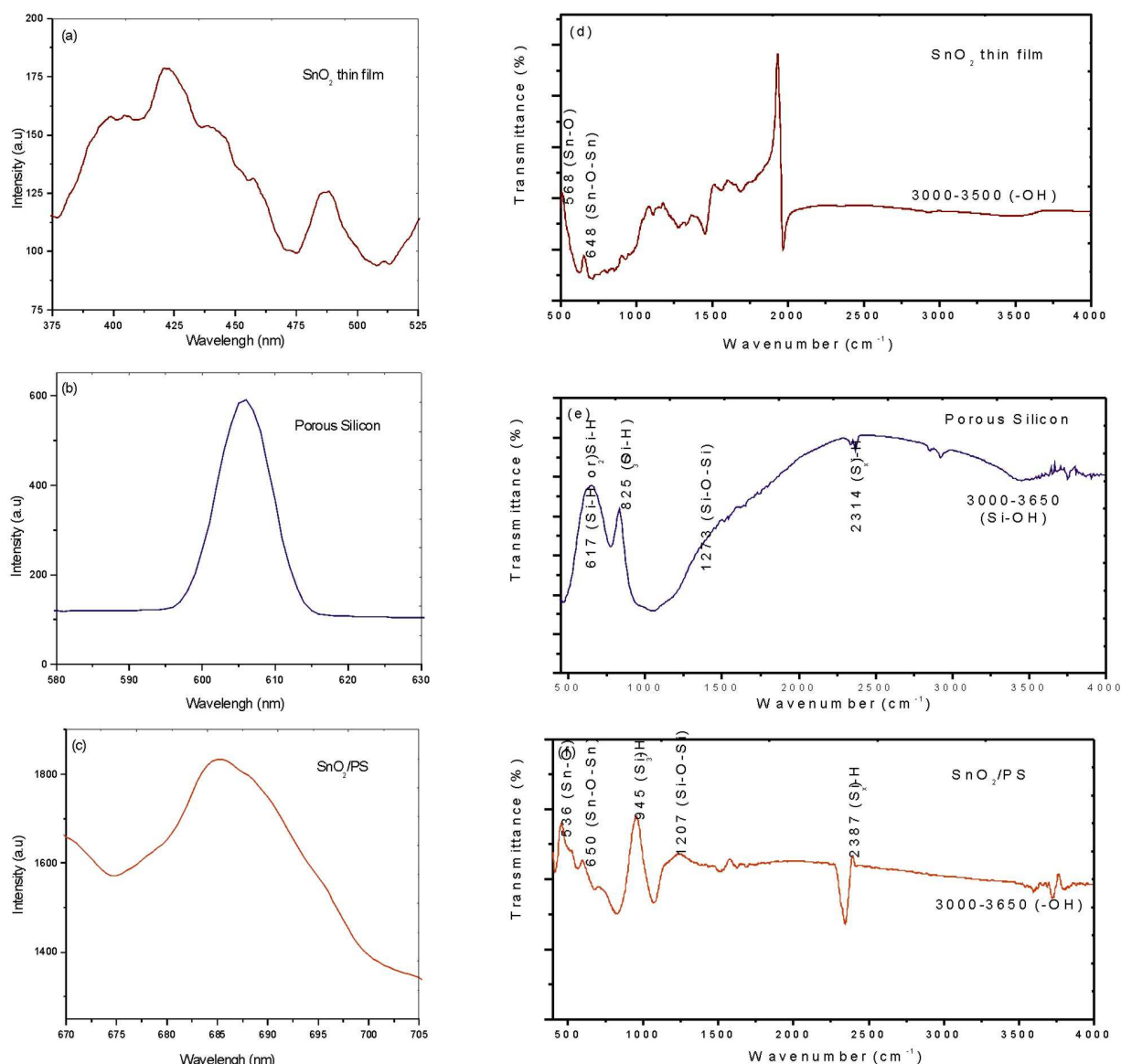


Figure 2 (a-c) PL and (d-f) FTIR spectra of SnO₂ tin film, PS and SnO₂ / PS

FTIR analysis has been used to detect chemical composition of the samples and the transmittance spectra of SnO₂ thin film (d), PS (e) and SnO₂/PS heterojunctions (f) were shown in Figure 2. The FTIR spectrum of SnO₂ thin film presents information about phase composition as well as about the oxygen bound metal ions (M-O structure). Figure 2 (e) shows very distinct sharp vibrational bands at 568 and 648 cm⁻¹ which may be attributed to Sn-O and Sn-O-Sn (belonging to Sn-OH groups) stretching vibrations respectively.

The FTIR spectrum of PS layer shows strong and weak bands at 617, 825, 1273, 2314 and 3000-3650 cm⁻¹ which are associated with Si-H (or) Si-H₂ wagging (or) deformation, O₃SiH, Si-O-Si, Si-H_x and Si-OH vibrations respectively. The presence of hydrogen complexes on PS surface has been suggested to explain the observed PL of PS. This can be taken to mean that the surface passivation plays a major role in determining the radiative efficiency of the porous layer. After deposition of the SnO₂ thin film, the covalently grafted inorganic molecules on silicon surfaces are confirmed by transmission FTIR spectra.

Figure 3 illustrates the schematic representations of SnO_2 thin films coated on PS substrate by sol-gel spin coating method and the characterization studies of tin oxide/porous silicon heterojunction in view of optoelectronics applications.

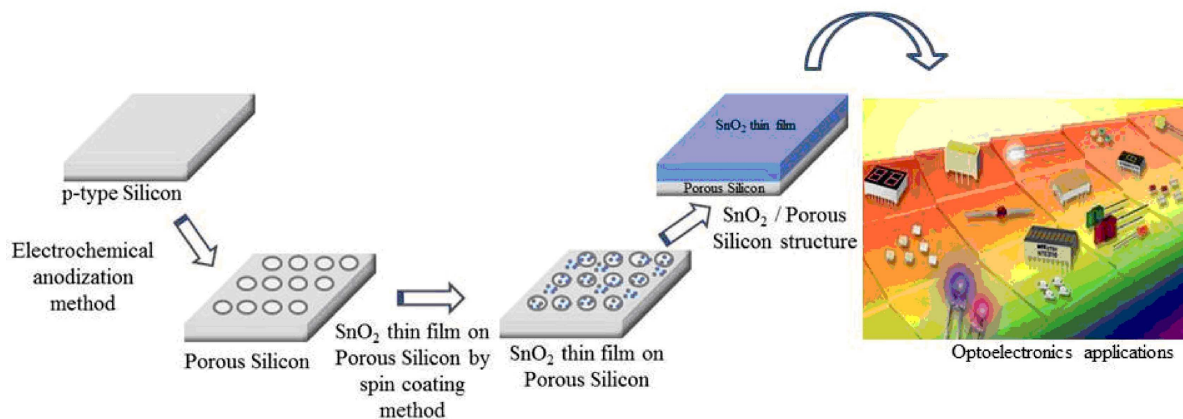


Figure 3. SnO_2 /PS structure for optoelectronic application.

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