CHAPTER – II

REVIEW ON POROUS SILICON (PSi) MATERIALS AND TRANSPARENT CONDUCTING OXIDES (TCOs)

2.1 INTRODUCTION

Transparent conducting oxide (TCO) thin films have figured prominently for many years in a wide variety of applications, such as heating elements on aircraft windows for deicing and defogging, antistatic coatings on instrument panels and electrical contacts in liquid crystals, electronic and electroluminescent displays. The high reflection in the infrared region, in conjunction with high transparency in the visible region, has been exploited to make heat-reflecting mirrors. The renewed research interest in these films in recent years stems from the possibility of fabricating large area, stable, and high-efficiency silicon based solar cell utilizing these films. Recently, to increase the junction area and reduce material cost, porous silicon (PSi) structures are developed and TCO/PSi gas sensors are under intense research.

A variety of techniques have been employed to deposit transparent conducting oxides. These include DC, RF and ion beam sputtering, ion plating, spray pyrolysis, sol-gel spin coating, CVD, electron beam and vacuum evaporation. PSi structures are formed by electrochemical and chemical routes. In this chapter, the formation and various physical and chemical properties published by various researchers for PSi, SnO₂, ZnO and PSi/semiconductor oxide based gas sensors are reviewed.

2.2 LITERATURE REVIEW ON FORMATION OF POROUS SILICON (PSi)

An enhancement in inelastic light scattering intensity from porous-silicon quantum wires has been discovered by M. E. Kompan et al [1]. It is shown that this effect is caused by a decrease in the absorption coefficient of the optical medium formed by quasi-one-dimensional structures, with the crystal structure of the wires themselves remaining unchanged.

The crystallite sizes, the bandgap energies, and the photoluminescence (PL) energies in porous silicon (PSi) samples having a wide range of porosities and kept in different ambient conditions was measured by J. Von Beheren et al [2]. The dependence of the bandgap energy on the crystallite size agrees with theory. For PSi samples exposed to air and containing crystallites smaller than 5 nm, the PL intensity increases by several
orders of magnitude and the PL peak energy shifts from the near infrared to the red, in agreement with the quantum confinement model for the PL. For crystallites smaller than 3 nm, there is a Stokes shift between the excitonic bandgap and PL energies, which increases to several hundreds of meV for sizes < 2 nm, indicating that, in PSi exposed to air, the PL is not due to free excitons. Before exposure to air, very high porosity PSi samples emit at shorter wavelengths than after exposure to air, suggesting that the Stokes shift depends on the surface chemistry.

E. A. Starostina et al [3] synthesized porous silicon by anodic etching in HF and ethanol electrolyte. The insitu current voltage characteristics clearly identify the pore formation, transition and electropolishing regimes. The experimentally observed impedance and phase as a function of frequency (Bode plots) reasonably agree with the theoretically simulated Bode plots drawn by considering the equivalent circuit for PSi/electrolyte.

The chemical formation of porous silicon in HF–HNO₃–H₂O etchants was studied by M.Ohnukai et al [4]. A technique is devised to determine the ranges in which the proportions of the acids should be varied in order to change from etch polishing to pore formation. The structure and properties of porous layers are examined in relation to the proportion of etchant ingredients.

Current-Voltage studies were carried out to get a better understanding of the mechanism of formation of porous silicon by F.V. Voloshina et al [5]. It is observed that on decreasing then anodization current below 75 mA cm⁻², the size of the PSi crystallites increase, while for a value above this current density electropolishing occurs. Raman spectroscopic studies show that the sizes of the Si crystallites are small and change from 4.7–3.8 nm when the current densities are increased from 20 to 50 mA cm⁻². Transmission electron micrographs show preferential propagation of pores whereas transmission electron diffraction patterns show the crystalline Si with the cubic structure.

The preparation of porous silicon at low HF concentrations using pulsed electrochemical method was studied by X. Shi et al [6]. The porous silicon was obtained at 5% HF concentration. By using pulse field, the total dissolution rate was higher than that of oxide formation at low HF concentration due to the dissolution rate of SiO₂ being enhanced giving porous silicon. Meanwhile the oxide film could become thicker due to the high hole density at high electric field and it resulted in the increasing of average pore size at low HF concentration of high etching current density.
The stability of porous silicon samples after thermal oxidation, thermal carbonization, thermal nitridation and dodecene treatment were compared. The stability of the samples in different temperatures was examined by C. Sanjay et al [7]. The reactivity of the stabilized porous silicon samples. EtOH and KOH solution at 25 °C was measured in an isothermal microcalorimeter. Other important properties of stabilized porous silicon samples for sensing applications such as specific surface area and humidity absorption behavior also were compared.

A composite device for sensing NO₂ vapours was formulated using metallophthalocyanine (MPc) with porous Si (PSi) by C. Ferrero et al [8]. Thin films of MPc were coated onto the surface of PSi and the surface resistivity was observed to change with exposure to vapours of NO₂. The superiority of this complex sensor is discussed in comparison with the single film sensor.

Electrical conductivity of porous silicon fabricated from heavily doped p-type silicon is very sensitive to NO₂ even at concentrations below 100 ppm have studied by G. Zeno et al [9]. However the sensitivity depends on the porous microstructure. The structural difference between sensitive and insensitive samples is independently confirmed by microscopic images and by light scattering behavior. A way to change the structure is by modifying the composition of the electrochemical solution. The best results were achieved using ethanoic solutions with HF concentrations between 12 and 13%.

Porous silicon exhibits extremely rich morphological features resulting from a set of very complex reaction processes at the silicon/electrolyte interface was studied by X. G. Zhang [10]. Numerous theories have been proposed since its discovery more than four decades ago, but there is still a lack of complete understanding of the formation mechanisms with respect to the observed morphological details. This paper attempts to provide a conceptual analysis of the various aspects in the morphology and formation mechanisms of porous silicon in light of currently available information on the fundamental reaction processes on silicon electrodes.

Photoluminescence (PL) measurement on porous Si (PSi) is carried out to investigate the inter defects by N. Korsunskka et al [11]. This article presents experimental results supporting the role of the ballistic transport in strong “red” PL of porous silicon. It is shown that this PL band connects with emission of oxide-related defects at the Si/SiOₓ interface. Also, the activation energy of the electrons is confined in
the PSi, as obtained from the temperature-dependent PL spectra. The activation energies of the electrons confined in PSi A peak and B peak were 67 and 61 meV, respectively.

A gas-based etching method for the fabrication of porous silicon was developed by A. Korcala et al [12]. It consists of exposing silicon samples to a mixture of oxygen (O₂) and nitrogen dioxide (NO₂) gases, and hydrogen fluoride (HF) and water vapors. The morphology, structure, porosity, photoluminescence properties, refractive index, and extinction coefficient of the porous layers, for various O₂:NO₂ flow rate ratios were investigated. The porous layers were characterized by island-like structures, attributed to the condensation of etchant-laden drops. Sections of porous silicon, with an average porosity and thickness of 88% and 1230 nm, respectively, were dispersed within a porous silicon matrix characterized by an average porosity and thickness of 79% and 301 nm, respectively. In addition to the striking difference in thickness between the islands and matrix, the morphology of the porous layer surface was different between the two areas. The size and density of the islands were found to strongly depend on the O₂:NO₂ flow rate ratio. Furthermore, the porous layers demonstrated a strong photoluminescence emission at an average peak wavelength of 658 nm.

The photoluminescence (PL) of as prepared porous silicon (PSi) etched in different time were studied by P. Banerji [13]. The variation of PSi blue emission was similar with that of Si complexes vibration mode on PSi surface so blue emission may be related to the defect states of surface Si complexes and hydrogen atoms on PSi surface can remove irradiative centers and result in increasing PL intensity. The peak centered at 570 nm may be associated to the emission of porous polycrystalline silicon in PSi surface, which can be proved by X-ray powder diffraction (XRD) and electron diffraction (ED) methods.

The porous silicone (PSi) is a relatively new and promising semiconductor material with special physical and chemical properties which somewhat differ from the properties of single crystal Si have investigated by M. Balarin et al [14]. Some of these properties are valuable in the field of gas sensor technology, but a lot of questions arise in connection with its application. The main target of this article is to give a short, but still comprehensive review of the application of the PSi layers on the field of the gas sensor technology, with special care on electrical output signal giving sensors.

J. Mizsei have studied [15] the photoluminescence (PL) properties of porous silicon (PSi) as a function of time. Stabilization of PL from PS has been achieved by replacing silicon–hydrogen bonds terminating the surface with more stable silicon–
carbon bonds. The composition of the PSi surface was monitored by transmission Fourier transform infrared (FTIR) spectroscopy at intervals of 1 month in ageing time up to 1 year. The position of the maximum PL peak wavelength oscillates between a blue-shift and a red-shift in the 615–660 nm range with time.

A new technique for porous silicon formation based on pulsed current anodic etching was studied by Be. Mahmoudi et al [16]. The technique offers the possibility of fabricating luminescent material with selective wavelength emission depending on cycle time (T) and pause time (T_{off}) of pulsed current during the etching process. Nanostructural nature of the porous layer has been demonstrated by X-ray diffraction (XRD) analysis and confirmed by photoluminescence (PL) and Raman spectroscopy. PL measurements of pulsed anodic etching porous silicon showed variety of emission wavelengths with strong intensity. Raman scattering from the optical phonon in porous silicon showed the red shift of the phonon frequency, broadening and increased asymmetry of the Raman mode with increasing T_{off}. Using the phonon confinement model, the average diameter of Si nanocrystallites has been estimated from 3.5 to 5.3 nm. Both is obtained between the results from PL and Raman spectroscopy of the etched Si samples.

Modelling and determining the electrical conductivity of nano-porous silicon (nano-PSi) films was studied by N. K. Ali et al [17]. The latter were prepared by electrochemical etching monocrystalline silicon (c-Si) wafers in HF-based solutions for different values of the anodic current. The experimental values of the dc-electrical conductivity of nano-PSi films were obtained using the dark current–voltage (I–V) characteristic of an Al/nano-PSi/c-Si/Al type structure. The electrical conductivity of the PSi films was theoretically estimated using the Bruggeman effective medium approximation (EMA) theory and by considering quantum size effects in small silicon particles. We give a comparative study between two different approaches. In the first one, we assume the PS layer to be formed of three phases: vacuum, oxide and c-Si nanocrystallites having the same mean size dimension (mean size value). In the second approach, we consider the nanocrystallites as being formed of multiple crystalline phases, depending on their size dimension. As a result, we found that in the case of the first simple approximation (three simple phases), theoretical data fit well the experimental results for small and medium porosities, and a discrepancy appears for porosities greater than 65%. However, in the case of multiple phases, theoretical values fit very well the experimental results for all porosities.
The electric behavior of porous silicon (PSi) thin films when the material's surface is exposed to carbon monoxide was studied by J. Torres et al [18]. PSi thin films were fabricated by the electrochemical anodization method of Si-c (100) substrates with resistivity 0.01 ohm cm. The samples were prepared at 20 min anodization time and 5 mA/cm² anodization current. Aluminum electrodes were deposited on the surface of the material by high vacuum evaporation, such that the electric conduction was parallel to the substrate's surface. The detector was placed in vacuum during 1 h and then CO was allowed into the vacuum chamber. Measurements of the I–V characteristic were carried out at atmospheric pressure, in vacuum and with CO. Changes in the resistance of the material, of about MΩ, were observed in the different samples, indicating that the material is sensitive to the presence of CO and therefore suitable as gas sensor.

The effect of surface passivation in porous silicon (PSi) as a hydrogen gas sensor was investigated by T. L. Sudesh et al [19]. Two types of sample have been prepared, one with typical HF anodizing solution and the other with the presence of peroxide (H₂O₂) in the solution. The Fourier transform infrared (FT-IR) measurements on the PSi layer on the Si substrate showed that the typical PSi surface is characterized by chemical species like Si–H and Si–O. Samples anodized with peroxide based (H₂O₂) solution showed a PS structure with higher porosity (~80%) and better surface passivation (higher concentration of Si–O and Si–H species) compared to those not treated with peroxide. Peroxide based PSi sample fabricated as an H₂ gas sensor showed better electrical (I–V) sensitivity compared to those without peroxide, which has been associated with good surface passivation. Surface passivation in peroxide based PS is also maintained at higher temperatures (100 °C).

2.3 LITERATURE ON PREPARATION AND CHARACTERIZATION OF SnO₂

A. F. Khan et al [20] prepared Tin oxide (SnO₂) thin films by rf-magnetron sputtering and annealed at various temperatures in the range of 100–500 °C for 15 min. Raman spectra of the annealed films depict the formation of a small amount of SnO phase in the tetragonal SnO₂ matrix, which is verified by x-ray diffraction. The average particle size is found to be about 20–30nm, as calculated from x-ray peak broadening and SEM images. Various optical parameters such as optical band gap energy, refractive index, optical conductivity, carrier mobility, carrier concentration etc. are determined from the optical transmittance and reflectance data recorded in the wavelength range 250–2500 nm.
Nanostructured tin oxide has been synthesized by O. A. Fouad [21] in one-step process by a novel simple thermal reduction-oxidation route. The results show that tin oxide nanowires and nanorods could be synthesized via thermal treatment of a mixture of tin oxide and charcoal powder in air at 1000-1250 °C. At a relatively low temperature, 1000 °C, and time, 30 min, the tin oxide structure was found to be a bundle of dense nanorods. By increasing the reaction time to 180 min at the same temperature (1000°C), the bundles separated to form liberated individuals nanowires with almost round cross-sectional view. With the increase of temperature and time, the morphology of tin oxide nanostructures varied from nanowires to well-defined tetragonal rods.

S. T. Chang et al [22] deposited tin oxide thin films by electrodeposition technique. Amorphous phase of the as-deposited film was obtained at the temperature of 85 °C. Nanocrystalline SnO2 having tetragonal structure with a grain size in the range of 4 to 7 nm was obtained by heat-treatment at 400 °C in a vacuum for 4 h. Porous, dense, and uniform morphologies for the deposits can be obtained by controlling current density during deposition. Results of infrared spectra, X-ray diffraction, scanning electron microscopy, and transmission electron microscopy analyses were described and correlated with the process of deposition and characteristics of the resulting SnO2 films.

Tin dioxide thin films prepared by sol-gel dip-coating method with ammonia treatment have been studied by Z. Gu et al [23]. By using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy, detailed investigation on the structure and morphology of the films has shown the condensation of Sn-OH and the strengthening of gel network net through ammonia treatment, which leads to the improvement of the adhesion of the films. From the spectral transmission, angular distribution of reflectance and absorption spectrum, the optical properties of the ammonia treated films indicate that the ammonia treated films have a favorable optical performance, and the films are more suitable for acting as antireflective films than the heat-treated films. The ammonia treated films also exhibit higher conductivity compared with the non-treated films.

J. Zhang et al [24] have been synthesized nanocrystalline SnO2 particles by a sol–gel method from the very simple starting material granulated tin. The synthesis leads a sol-gel process when citric acid is introduced in the solution obtained by dissolving granulated tin in HNO3. Citric acid has a great effect on stabilizing the precursor solution, and slows down the hydrolysis and condensation processes. The obtained SnO2 particles range from 2.8 to 5.1 nm in size and 289–143 m²g⁻¹ in specific surface area when the gel
is heat treated at different temperatures. The particles show a lattice expansion with the reduction in particle size. With the absence of citric acid, the precursor hydrolyzes and condenses in an uncontrollable manner and the obtained SnO$_2$ nanocrystallites are comparatively larger in size and broader in size distribution. The nanocrystallites have been characterized by means of TG-DSC, FT-IR, XRD, BET and TEM.

M. Bhagwat et al [25] reported that preparation of SnO$_2$ powder by liquid mix technique using citric acid as the complexing agent. The tin oxide powder obtained at different calcination temperatures (773–1223 K) is characterized using powder X-ray diffraction (XRD), SEM, TEM, TG-DTG and UV spectroscopic techniques. The material obtained is nanocrystalline, having particle size in the range of 10–14 nm. The technique is cost-effective and yields the desired product at temperatures as low as 773 K.

Tin oxide nanowires have been grown on p-type silicon substrates using a gold-catalyst-assisted vapor–liquid–solid growth process by A. Kar et al [26]. The nanowires were annealed in the presence of oxygen at 700 °C for different time intervals. The changes in material properties of the nanowires after annealing were investigated using various characterization techniques. Annealing improves the crystal quality of the nanowires as seen from Raman spectroscopy analysis. Photoluminescence (PL) data indicates a decrease in the oxygen vacancies and defects after annealing, affecting the luminescence from the nanowires. In addition, x-ray photoelectron spectroscopy (XPS) was used to obtain the changes in the tin and oxygen atomic concentrations before and after annealing, from which the stoichiometry was calculated.

N.G. Deshpande et al [27] prepared SnO$_2$ nanocrystalline thin films onto glass substrates by a Modified Successive Ionic Layer Adsorption and Reaction technique at room temperature. The deposition parameters were optimized and the films were annealed in oxygen atmosphere (500 °C, 1 h). The obtained (as-deposited and annealed) thin films were characterized for structural, optical and electrical properties. X-ray diffraction patterns revealed that the films were either nanocrystalline and/or amorphous in nature with cassiterite tetragonal structure. Atomic force microscopy studies showed uniform grain distribution with average grain size found to be increased from 86 nm for as-deposited to 94 nm for the annealed samples. Optical band gap (3.62 eV) for as-deposited samples was decreased to 3.51 eV after annealing. A decrease in photoluminescence intensity was observed after annealing. Schottky junction of SnO$_2$ with silver has been made and barrier height (0.51 eV) was determined using current-
voltage characteristics. The junction gave good response on illuminating it with 150 mW cm\(^{-2}\) light intensity.

M. Risti et al [28] have prepared very fine SnO\(_2\) powders by (a) slow and (b) forced hydrolysis of aqueous SnCl\(_4\) solutions and (c) hydrolysis of tin(IV)-isopropoxide dissolved in isopropanol (sol-gel route) and then characterized by X-ray powder diffraction, Fourier transform infrared and laser Raman spectroscopies, TEM and BET. The XRD patterns showed the presence of the cassiterite structure. TEM results also showed that the sizes of SnO\(_2\) particles in all powders are in nanometric range. The broad Raman band at 571 cm\(^{-1}\) was ascribed to amorphous tin(IV)-hydrous oxide. The additional Raman bands at 500, 435 and 327 cm\(^{-1}\) were recorded for nanosized SnO\(_2\) particles produced by forced hydrolysis of SnCl\(_4\) solutions. On the basis of these measurements it was concluded that the size of SnO\(_2\) particles was also in the nanometric range and that, the sol–gel particles heated to 400 °C consisted of several SnO\(_2\) crystallites.

Z. Jie et al [29] prepared SnO\(_2\) thin films by dip-coating from SnO\(_2\) sols of 0.5 and 0.1 mol/l. The structure and morphology of the films were analyzed through XRD, UV and AFM methods. The particles in the films were the standard tetragonal phase of SnO\(_2\) with spherical morphology. The average size of SnO\(_2\) particles was about 87 nm (0.5 mol/l) and 5 nm (0.1 mol/l), respectively. The UV absorbance of the films increased linearly with increasing the deposition layers. The sensitivity of thin films to methanol, ethanol, propanol and acetone was detected at room temperature, and the effects of concentration of SnO\(_2\) sols on the morphology and sensitivity of the films were investigated as well. With decreasing the sol concentration, the grain size of the particles reduced, the gas sensing properties to acetone and ethanol increased. Such films with small size could detect ethanol as low as 2 ppm ethanol. Response and recovery time to methanol, ethanol, propanol and acetone at room temperature were within 30 s and 1 min, respectively.

F. Gu et al [30] have reported that nanometer-scale SnO\(_2\) particles have been synthesized by a simple sol–gel method. The samples were characterized by X-ray diffraction, Fourier transform infrared (FTIR), UV–Vis absorption and photoluminescence spectroscopy. The as-prepared SnO\(_2\) nanoparticles appear to be single tetragonal crystalline phase and the diameter is about 2.6 nm. The origin of luminescence is assigned to the recombination of electrons in singly occupied oxygen vacancies with photoexcited holes in the valence band.
A. Sharma et al [31] were using thermal evaporation technique for nanocrystalline tin oxide thin films. The grain sizes, crystallization process and morphology were investigated by X-ray diffraction (XRD) and Atomic Force Microscopy (AFM). Both optical band gap and transmittance were enhanced after heat treatment. All IR modes measured by Fourier Transform Infrared Microscopy (FTIR) spectrometer were assigned. The FTIR spectra show an increase in the intensity of the Eu mode (606.75 cm\(^{-1}\)) after post annealing, which indicates fine crystallization of SnO\(_2\) grains. Thermal treatment induced defects enhance the diffusion of atoms leading to uniformity in size of grains. But the grains were found to be elongated and larger in size, in case of SnO\(_2\) films on quartz substrate deposited. The role of substrate on thermal treatment induced grain growth process was discussed.

2.4 LITERATURE ON PREPARATION AND PROPERTIES OF ZnO

The compositional, structural, microstructural, DC electrical conductivity and optical properties of undoped zinc oxide films prepared by the sol–gel process using a spin coating technique were investigated by V. B. Patil et al [32]. The ZnO films were obtained by 5 cycle spin-coated and dried zinc oxide films followed by annealing in air at 600 °C. The films deposited on the platinum coated silicon substrate were crystallized in a hexagonal wurtzite form. The energy-dispersive X-ray (EDX) spectrometry shows Zn and O elements in the products with an approximate molar ratio. TEM image of ZnO thin film shows that a grain of about 60 – 80 nm in size is really an aggregate of many small crystallites of around 10 – 20 nm. Electron diffraction pattern shows that the ZnO films exhibited hexagonal structure. The SEM micrograph showed that the films consist in nanocrystalline grains randomly distributed with voids in different regions. The DC conductivity found in the range of 10\(^{-5}\) – 10\(^{-6}\) (Ω cm\(^{-1}\)). The optical study showed that the spectra for all samples give the transparency in the visible range.

Y. Y. Kim et al [33] reported the structural and optical properties of ZnO thin films grown on Si substrates were investigated for different growth temperatures in the range of 520 – 720 °C. X-ray diffraction investigations revealed the preferred c-axis oriented growth of ZnO thin films, which was further confirmed by the presence of ZnO (002) diffraction spots with arc shape. The increase in growth temperature transformed surface morphology from pyramidal with columnar grains to relatively flat surface with increased grain size. In addition, the increased growth temperature caused red shift and
intensity enhancement of band-edge emission of the ZnO, which were related to the increase in tensile strain and the grain size, respectively.

A. A. Ibrahim et al [34] prepared the ZnO/Si heterojunctions by depositing n-ZnO films doped with aluminium on p-Si by spray pyrolysis method. Heterojunction solar cells were fabricated using the configuration Al/ZnO/Si/In. The electrical properties of the heterojunction are investigated by means of current-voltage measurements in the temperature range 295–375 K. The cells show the rectifying behaviour characterized by the current–voltage (I–V) measurement under a dark condition, while photoelectric effects have been exhibited under the illumination. As a result, the conversion efficiency of the fabricated cell of about 6.6% was obtained.

The optical constants and optical band gaps of the non-crystalline and crystalline zinc oxide (ZnO) thin films deposited by the spray pyrolysis method onto glass substrates at the different deposition times have been investigated by F. Yakuphanoglu et al [35]. The structure of the films was analyzed by X-ray diffraction and the results obtained showed that the film structure changed from non-crystalline to crystalline with increasing the deposition time. The effect of film thickness on the band gap and optical constants (refractive index, extinction coefficient and dielectric constants) of these films has been investigated and the film thickness changes the optical constants and Urbach energy values of the films. The direct band gaps $E_g$ of ZnO thin films with different thickness were 3.28 - 3.29 eV. It can be evaluated that the film thickness does almost not change the optical band gap of the films. The width of the tails of localized states in the optical band gap of the films increases with increasing non crystalline film thickness. The dispersion curves of the refractive index of the non crystalline films obey single-oscillator model, whereas the curves of the crystalline films do not obey this model. The dispersion parameters such as $E_o$ (single-oscillator energy) and $E_d$ (dispersive energy) of the non crystalline films were determined. These values increase with increasing film thickness.

X.Q. Wei et al [36] prepared zinc oxide thin films by pulsed laser ablation of a ZnO target in O$_2$ ambient at a pressure of 0.13 Pa using a pulsed Nd:YAG laser. ZnO thin films deposited on Si (111) substrates were treated at annealing temperatures from 400 °C up to 800 °C after deposition. The structural and optical properties of deposited thin films have been characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, photoluminescence spectra, resistivity and IR absorption spectra. The results show that the obtained thin films possess good single crystalline with hexagonal structure at annealing temperature 600 °C. Two emission peaks have been
observed in photoluminescence spectra. As the post-annealing temperature increase, the UV emission peaks at 368 nm is improved and the intensity of blue emission at 462 nm decreases, which corresponds to the increasing of the optical quality of ZnO film and the decreasing of Zn interstitial defect, respectively. The best optical quality for ZnO thin films emerge at post-annealing temperature 600 °C in our experiment. The measurement of resistivity also proves the decrease of defects of ZnO films. The IR absorption spectra of sample show the typical Zn–O bond bending vibration absorption at wavenumber 418 cm⁻¹.

J.Y. Lee et al [37] reported that the fabrication of n-ZnO/p-Si heterojunction photodiodes. RF sputtering was performed to deposit ZnO films on p-Si substrates at various substrate temperatures of 300, 480 and 550 °C using Ar:O ratios of 6:1. Typical 2 rectifying behaviors were observed from most of the diodes as characterized by the current–voltage (I–V) measurement. Some of the diodes exhibit photoelectric effects under illumination using monochromatic red light with a wavelength of 670 nm. Maximum quantum efficiency of 53% was obtained under a reverse bias condition from a diode with ZnO film deposited at 480 °C. Measuring photoluminescence, transmittance, sheet resistance from the ZnO films, and characterizing the n-ZnO/p-Si interface with X-ray photoelectron spectroscopy, it is concluded that the diodes with n-ZnO deposited at 480 °C conserve relatively a high film quality and good interface junction to exhibit the best photoelectric property.

ZnO thin films on Si (111) substrate were deposited by laser ablation of Zn target in oxygen reactive atmosphere; Nd-YAG laser with wavelength of 1064 nm was used as laser source. The experiments were performed by X. M. Fan et al [38] at laser energy density of 31 J/cm², substrate temperature of 400 °C and various oxygen pressures (5–65 Pa). X-ray diffraction was applied to characterize the structure of the deposited ZnO films and the optical properties of the ZnO thin films were characterized by photoluminescence with an Ar ion laser as a light source using an excitation wavelength of 325 nm. The influence of the oxygen pressure on the structural and optical properties of ZnO thin films was investigated. It was found that ZnO film with random growth grains can be obtained under the condition of oxygen pressure 5–65 Pa. It will be clearly shown that the grain size and the formation of intrinsic defects depend on the oxygen partial pressure and that high optical quality of the ZnO films is obtained under low oxygen pressure (5 Pa, 11 Pa) conditions.
W.W. Dong et al. [39] reported the influence of homo-buffer layers deposited at high-temperature (HT) or low-temperature (LT) and post-annealing process on the structure and photoluminescence properties of ZnO films grown by pulsed laser deposition on Si (100) was studied by X-ray diffraction (XRD), atomic force microscope (AFM) and photoluminescence spectrum (PL). It is found that the optical property of the films can be improved greatly because the stress between the films and the substrates could be reduced by using buffer layers. By using LT buffer layer, high-quality ZnO films with only one strong ultraviolet emission (UV) can be obtained, but the post-annealing process in air will make the optical property of the film deteriorate.

Nanocrystalline ZnO films with preferred c-axis orientation are grown under varying oxygen partial pressure by K. C. Dubey et al. [40]. The crystalline quality decreases at lower oxygen partial pressure whereas the lattice constant increases. The optical band gap is determined to be \( \sim 3.27 \) eV from the transmittance data. The ZnO films when subjected to repeat heating and cooling cycles at temperatures below the deposition temperature their properties get modified. Comparison between the diffraction peak position, interplanar spacing, lattice constant, FWHM, grain size, optical band gap and electrical resistivity before and after cyclic heat treatment of the films is done. The sharp absorption edge of the film deposited at higher oxygen pressure shows a small red shift after heat-treatment leading to a change of 0.04 eV in the optical band gap. The resistivity of film deposited at higher oxygen partial pressure reduces to half whereas that of deposited at lower pressure reduces to one-fifth after the heat-treatment.

Nanocrystalline ZnO thin films deposited onto silicon substrates by sol-gel technique were studied by C. Shaoqiang et al. [41]. The starting material for ZnO sol-gel thin films was Zinc acetate. Single crystalline silicon wafers with different orientations and the porous silicon substrates were used as the substrates. XRD was employed to investigate the evolution of the crystalline orientation during the thermal treatment, and SEM was used to observe the surface morphology of the ZnO films. The effects of the annealing temperature and the substrate doping type on the deposited ZnO thin films were studied in detail. The results indicated that the highly oriented ZnO could be generated on Si substrates by controlling the process conditions. It was found that the substrates types had less influence on the obtained ZnO thin films compared with the annealing temperatures. Thin porous silicon substrates introduced is beneficial to enhance the bonding strength between the films and the substrates. These results are helpful to
deposit the highly orientation-controlled ZnO thin films for different kinds of research and application.

H. Cai et al [42] investigated the ZnO/PSi nanocomposite films. The porous silicon (PS) substrates were formed by electrochemical anodization from p-type (100) silicon wafer, and the starting material for ZnO was Zinc acetate. The ZnO thin films were deposited on the PSi substrate with different porosities by sol-gel spin coating technique. XRD analysis revealed that highly (002) oriented ZnO thin films were formed. The photoluminescence (PL) measurements on the ZnO/PSi nanocomposite films showed three intense broadband photoluminescence emissions at around ~ 380 nm, ~ 510 nm, and ~ 750 nm. The effects of the PS substrate on the PL properties were also studied in detail.

Zinc oxide (ZnO) nanowire arrays with controlled nanowire diameter, crystal orientation, and optical properties were prepared on sol-gel ZnO-seed-coated substrates with different pretreatment conditions by a hydrothermal method was discussed by J.S. Huang and C.F. Lin [43]. The vertical alignment, crystallinity, and defect density of ZnO nanowire arrays are found to be strongly dependent on the characteristics of the ZnO thin films. Field-emission scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, and room temperature photoluminescence were applied to analyze the quality of the ZnO nanowire arrays. The annealing temperature of the ZnO thin film plays an important role on the microstructure of the ZnO grains and then the growth of the ZnO nanowire arrays. The X-ray diffraction results indicate that the thin film annealed at the low temperature of 130 °C is amorphous, but the thereon nanowire arrays are high-quality single crystals growing along the c-axis direction with a high consistent orientation perpendicular to the substrates. The as-synthesized ZnO nanowire arrays via all solution-based processing enable the fabrication of next-generation nanodevices at low temperature.

X. D. Gao et al [44] have reported the transparent ZnO films were deposited on the ITO/glass substrates from zinc nitrate aqueous solution by the two-step electrodeposition technique. While the first potentiostatic step was used to produce ZnO seed layer, the ZnO film growth has been done galvanostatically. Effects of the potentiostatic parameters on the crystal structure, morphology and optical properties of ZnO films were investigated. Results show that ZnO films with highly c-axis preferred orientation can been obtained when the potentiostatic deposition at –1.2 V for 15 s has been applied. Such an observation might be attributed to the etching process of ITO substrate in the
diluted HCl solution. The film exhibits smooth and compact morphology, high transmittance in the visible region (>80%) and sharp absorption edge at ~370 nm. The analysis on the growth mechanism indicates that the short potentiostatic process prior to the film growth can produce ZnO seed layer and substitute the initial nucleation process in the conventional one-step galvanostatic deposition, thus increasing the nucleation density and preventing the formation of loose structures.

U. Alver et al [45] have prepared zinc oxide (ZnO) microrods at different substrate temperatures by ultrasonic spray pyrolysis technique on glass substrates. The X-ray diffraction patterns show that obtained rods are composed of wurtzite-type and mainly grow along the (002) direction. Scanning electron microscope images show that the diameters of ZnO rods and the distances among the rods increase with increasing substrate temperature. In addition, the optical measurements reveal that transmittance and the band gap energies of films increase with increasing substrate temperature.

2.5 LITERATURE ON SEMICONDUCTOR OXIDE/PSi BASED GAS SENSORS

A. Chiorino et al [46] prepared SnO$_2$ powders pure and added with W$^{6+}$ at two different loadings (1 and 5 W mol%) via a sol-gel route. Thick films prepared from the powders were used as CO and NO$_2$ gas sensors. The morphology of the powders was analyzed by TEM, HRTEM and that of films by SEM. The goal of obtaining powders and films made by nanosized particles, even after thermal treatments at 850 °C was attained. The effect of W on the response of powders and films towards CO and NO$_2$ was studied by FT-IR and conductance measurements, respectively. Surface species formed by CO and NO$_2$ interaction were investigated.

Z. Jiao et al [47] reported the effects of electron beam irradiation on the gas sensing performance of tin dioxide thin films toward H$_2$ are studied. The tin dioxide thin films were prepared by ultrasonic spray pyrolysis. The results show that the sensitivity increased after electron beam irradiation. The electron beam irradiation effects on tin dioxide thin films were simulated and the mechanism was discussed.

M.N. Rumyantseva et al [48] have been measured Raman surface vibration modes for SnO$_2$ nanocrystalline powders with grain sizes of 3-36 nm and a specific surface area up to 180 m$^2$g$^{-1}$, which were prepared by four different routes of chemical synthesis. The influence on these surface vibration modes of the treatment temperature, the crystallite size, and the specific surface area has been studied and bands at 245, 257, 286, 310-350, and 400-700 cm$^{-1}$ have been identified. The 400-700 cm$^{-1}$ band intensity has been found...
proportional to the surface active area. Likewise, the correlation of the 400-700 cm$^{-1}$ band intensity with the sensing mechanisms have been analyzed from the sensor response of the prepared thick-film gas sensors against reducing CO and oxidizing NO$_2$ species diluted in a N$_2$ carrier. The influence of the nanostructure surface on the sensor signal exhibits opposite trends for CO than for NO$_2$ detection. As the Raman surface vibration modes, 400-700 cm$^{-1}$, band intensity increases, the sensor response for CO increases too, while that of NO$_2$ diminishes, giving an excellent inverse correlation between the sensor response for CO and NO$_2$. This correlation is fulfilled for all the samples except those that are distorted by the presence of an excess of contamination caused by OH$^-$ groups together with Cl$^-$ ions introduced by the chemical synthesis procedure.

S. G. Ansari et al [49] investigated the thick and thin films of SnO$_2$ are extensively used for resistive gas sensors. Characteristics are compared for films produced by four different techniques of chemical vapour deposition (CVD), spray pyrolysis, vacuum evaporation and screen printing. The films are characterized for H$_2$ sensing only, using a static measurement system to investigate their temperature selectivity. The samples are tested at a concentration of 300 ppm. No selective peak is observed for CVD and spray deposited samples, and the selective peak for vacuum evaporated samples has a low sensitivity. But the selective peak for screen printed samples has a sensitivity of 55%.

M.A. Dal Santosa et al [50] prepared the SnO$_2$ films by the modified sol-gel method, using tin tartrate as a precursor, are presented. The sol stability was verified using UV-visible spectroscopy. The obtained films were characterized by X-ray diffraction (XRD), optical microscopy, electrical measurements, scanning electron microscopy (SEM), and X-ray fluorescence (FRX). The obtained films presented a thickness of 0.3 μm and an amorphous structure. The sensor electrical sensibility at 300 °C in the presence of LPG was clearly shown.

R. Rella et al [51] prepared the pure and palladium-modified SnO$_2$ thin films by sol-gel technique for gas sensors application. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) techniques were used to analyse the structure, the chemical composition and the morphology of the prepared films. Pure tin oxide films have shown gas sensing characteristics similar to most of the SnO$_2$ films realized with other more expensive and more elaborate methods of preparation. Pd-doped SnO$_2$ films have shown an improvement in the sensitivity, probably due to the Pd catalytic effect and to the induced microstructural changes.
V.R. Shinde et al [52] have been prepared the nano porous ZnO films consisting of nano structural beads by pyrolytic decomposition of an aqueous zinc nitrate solution and their liquid petroleum gas (LPG) sensing properties were studied. The response of the ZnO nano beads towards LPG was enhanced significantly by palladium (Pd) sensitization which was deposited onto the ZnO nano beads by a sequential dipping and drying method. The LPG sensing properties of the ZnO nano beads and Pd-sensitized ZnO were investigated at different operating temperatures and different gas concentrations ranging from 0.1 to 0.4 vol%. The unsensitized ZnO nano beads exhibited the maximum response of 31% at 673 K upon exposure to 0.2 vol% LPG which was improved up to 63% at the optimum temperature of 548 K by Pd sensitization. Additionally, the Pd-sensitized ZnO was able to respond very quickly to the exposure of LPG.

M. Suchea et al [53] prepared the zinc oxide (ZnO) transparent thin films onto silicon and Corning glass substrates by DC magnetron sputtering using metallic and ceramic targets. XRD measurements have proven that the dc sputtered films are polycrystalline with the (002) as preferential crystallographic orientation. AFM analysis of thin films sputtered from a ceramic target has shown a completely different surface behavior compared with that of the films grown from a metallic target. This work demonstrates that the target material and the growth conditions determine the film surface characteristics. The gas sensing characteristics of these films are strongly influenced by surface morphology. Thus correlating the optical and electrical film properties with surface parameters (i.e. RMS and Grain Radius) can lead to an enhancement of the material's potential for gas sensing applications.

G. Sarala Devi et al [54] prepared zinc oxide nanoparticles using zinc acetate precursor by the sol-gel synthesis. The reaction product obtained before and after reflux of propanolic zinc acetate solution have been studied by UV–vis, photoluminescence and FT-IR studies which confirm the formation of oligomeric precursor Zn₄O(Ac)₆ (Ac=CH₃COO). The formation of zinc oxide nanoparticles were confirmed by X-ray diffraction (XRD) and Transmission electron microscopic studies (TEM). The gaseous ammonia gas sensing characteristics of the nano-zinc oxide sensor showed high sensitivity compared to sensor fabricated with commercial zinc oxide powder.

Vertically aligned ZnO nanorods, faceted microrods, nanoneedles and nanotowers were grown on glass substrates by a cost effective and low temperature aqueous chemical method by R.C. Pawar et al [55]. Various polymers viz. polyethylenimine (PEI), polyacrylic acid (PAA) and diaminopropane (DAP) were used as structure directing
agents. The aligned ZnO nanorod formation takes place with the predominant orientation along (002) plane. These nanocrystalline ZnO samples were used to explore gas response properties for acetone, ammonia, LPG and ethanol. It is observed that the sensors based on DAP-directed nanoneedles showed higher response (90%) for acetone gas at 275 °C. The high acetone gas sensitivity and low operating temperature of ZnO nanoneedles can be attributed to the surface morphology.

P. Mitra et al [56] prepared zinc oxide (ZnO) thin films by a chemical deposition technique using a sodium zinicate bath. Structural characterizations by X-ray diffraction (XRD) indicate the formation of ZnO film with a preferred c-axis orientation. The electrical conductance of the ZnO films became stable and reproducible in the 300 – 500 K temperature range with two activation energy barrier values of 0.3 eV and 0.8 eV in the low temperature (300 – 420 K) and high temperature (430 – 500 K) ranges, respectively. The ZnO films prepared by this method are highly resistive, indicating the presence of a large density of oxygen adsorbed acceptor-like trap states. Palladium doped ZnO films were exposed to hydrogen (H₂) with air as a carrier gas at different operating temperatures ranging between 150 – 375 °C and the response is evaluated.

SnO₂ sol-gel derived thin films doped simultaneously with Pt and Sb are obtained and reported by C. Savaniu et al [57]. The Sn sources were tin (IV) ethoxide or tin(II) ethylhexanoate, while hexachloroplatinic acid (H₂PtCl₆) and antimony chloride (SbCl₃) were used as platinum and antimony sources, respectively. Transparent, crack-free layers, deposited on silicon or porous silicon (PSi) substrates were obtained with antimony doping in the range (0 to 2)% M, while the platinum addition was limited to maximum 1% M, due to the strong acidic character of the Pt and Sb precursors. Ternary sol (Pt:Sb:SnO₂) stability was analysed by viscosity studies while the surface roughness of the doped SnO₂ layers on both types of substrates was investigated by atomic force microscopy (AFM) measurements. Rutherford Backscattering spectra (RBS) analysis proved that pores of PS substrates had been filled as a result of multiple spin-casting processes.

Columnar porous silicon (CPSi) substrate/SnO₂ gas-sensor devices with high sensitivities and low working temperatures (input power 500 – 800 mW in TO-99 casing) are presented by A. Dima et al [58]. The paper compares a conventional substrate (SnO₂ on SiO₂/silicon substrate) with two porous substrate devices, one with pores of 60–300 nm (‘porous’), and the other of 400–2000 nm (‘mesoporous’). The CPSi substrates were prepared on (100) p-type 3 inch silicon wafers through boron diffusion and anodisation.
The SnO$_2$ was prepared through sol-gel deposition from tin II ethylhexanoate precursors and was deposited through spin coating. The W/Au inter-fingered contact structure was deposited over the SnO$_2$ layers for the ‘porous’ and ‘mesoporous’ devices. The SnO$_2$ layers were vitrified layer-by-layer at 400 °C and at the end annealed at 500 °C. The results indicate a mid-range working temperature range (250 °C) for the ‘porous’ substrate device, with good response times and high sensitivity, relative to the SnO$_2$/silicon substrate device. The ‘mesoporous’ substrate device has yet higher sensitivity, however, it is considerably slower (typically 320 s OFF-times for O$_2$ in synthetic air).

D. D. Vuong et al [59] have reported that the colloidal dispersions of crystalline SnO$_2$ (sols) with a mean grain (crystallite) size controlled between 6 and 16 nm were prepared successfully from stannic acid gel by hydrothermal treatments under the condition of pH 10.5 and 200 °C or pH 12.2 and 250 °C. The growth of crystallites saturated in a few hours of hydrothermal treatment and the saturation values tended to increase with increasing SnO$_2$ gel content, pH and temperature. The SnO$_2$ grains remained monodispersed unless time of hydrothermal treatment was excessive. Thin films of SnO$_2$ prepared on alumina substrate from the sols by a spin-coating method responded sharply to H$_2$ gas. The magnitude of sensor response as well as its dependence on operating temperature were different significantly depending on the grain sizes of the starting sols. Among the sols with a mean grain size of 6, 8.5, and 10 nm, the last two gave large response to H$_2$, which reached a maximum at 400 or 350 °C, respectively.

V. M. Arakelyan et al [60] have prepared n-type TiO$_{2-x}$ and In$_2$O$_3$:SnO$_2$ thin films onto p-type porous silicon layer which was formed by common electrochemical anodization. The current-voltage characteristics of obtained structures and sensitivity to different concentrations of hydrogen in air were studied. Measurements were carried out at room temperature. As shown results of measurements, an exponential growth of the current in forward branch of the current-voltage characteristics of the device made of TiO$_{2-x}$ layer was detected. Higher sensitivity to hydrogen of the TiO$_{2-x}$-porous silicon sensor in comparison to structure made of In$_2$O$_3$:SnO$_2$ film was detected at room temperature (without preheating of work body of the sensor).

2.6 CONCLUSION

In this chapter, a detailed literature review on preparation and properties of porous silicon (PSi), SnO$_2$, ZnO and semiconductor oxide based sensors are presented.
REFERENCES


