

# **Growth and Characterization of Silicon Dioxide Thin Films Developed by Anodic Oxidation**

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## Declaration

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# Approval Sheet

This thesis entitled **Growth and characterization of silicon dioxide films developed by anodic oxidation** is approved for the degree of Master of Science in Physics from IIT Hyderabad.

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I am making this project not only for marks but to also increase my knowledge.  
THANKS AGAIN TO ALL WHO HELPED ME.

Dedicated to

**“My Family and Guide”**

## **Abstract**

Silicon dioxide ( $\text{SiO}_2$ ) is also known as silica, it is a chemical compound that is an oxide of silicon. Thin films of silicon dioxide are most widely used in the fabrication of silicon based integrated/discrete devices (e.g. diode, transistors, etc.), integrated circuits (ICs) and microelectromechanical systems (MEMS) fabrication for various purposes. The  $\text{SiO}_2$  layer has been used as surface passivation to protect semiconductor devices from contamination, gate dielectric in metal oxide semiconductors (MOS), mask against diffusion and implantation of dopants into silicon, dielectric in the storage capacitors of DRAM memories, isolating the devices from one another on the same chip, as sacrificial and etch mask layer in MEMS fabrication. Several techniques has been well established to prepare the silicon dioxide films in different processing environments, however Thermal oxidation, Sputtering, Chemical Vapor Deposition are most commonly used. Among the various existing techniques of silicon dioxide synthesis Anodic oxidation of silicon is one of the technique which can be operated even below room temperature. The Anodic oxidation process offers several advantages over other techniques such as low cost of process, simple experiment set up, does not involve any toxic and expensive gases, etc. The present work is aimed to investigate the effect of various parameters such as current density, final voltage, and composition of the electrolyte on different characteristics of the as-grown oxide films. Uniform and non-porous silicon dioxide thin films are obtained at small water content added into the electrolyte. The thickness of the oxide increases as the water content in the electrolyte increased. Various characterization tools such as Ellipsometry, SEM and FTIR are employed to characterize the thickness, refractive index, surface morphology and chemical composition of the as-grown oxide thin films.

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## 1. Introduction

Silicon dioxide is also known as silica it is a chemical compound that is an oxide of silicon with the chemical formula  $\text{SiO}_2$ . It is most commonly found in nature as quartz. The ability to form a chemically stable protective layer of silicon dioxide on the surface is one of the main reasons that makes silicon the most widely used semiconductor material in several fields. The oxidation of silicon to produce thin and high quality films is of scientific interest because of potential applications of  $\text{SiO}_2$  in different fields. The thin films of the  $\text{SiO}_2$  have been used as a barrier material during impurity implants or diffusion, for electrical isolation of semiconductor devices, as a component in the MOSFET (Metal Oxide Semiconductor Field Effect Transistor) and etch mask, sacrificial layer in MEMS fabrication. There are several ways to form  $\text{SiO}_2$  on the surface of silicon. Usually  $\text{SiO}_2$  film on silicon (substrate) produced either by growth or direct deposition based processes. The two pre-dominant methods are thermal oxidation and deposition of a thin film by chemical vapor deposition (CVD). The CVD techniques of  $\text{SiO}_2$  synthesis comprises Low Pressure Chemical Vapor Deposition (LPCVD), Atomic Pressure Chemical Vapor Deposition (APCVD) [1], Plasma Enhanced Chemical Vapor Deposition (PECVD) [2], similarly Plasma Vapor Deposition (PVD) comprises Sputtering [3], Thermal evaporation, etc. Thermal oxidation technique provide the high quality  $\text{SiO}_2$  film at temperature greater than  $850\text{ }^\circ\text{C}$ . However, high processing temperature ( $\sim 900\text{-}1100\text{ }^\circ\text{C}$ ) of this technique causes redistribution of dopants in silicon substrate during oxide growth and develop stress in silicon substrate that leads to wafer warpage [4, 6]. Using thermal oxidation  $\text{SiO}_2$  films can be grown by two different ways one is wet (water vapor as source of oxygen) process and another in dry (oxygen) atmosphere. But due to its high temperature growth it has some drawbacks such as redistribution of the impurity dopants in silicon wafer during oxide growth, minority carrier life time is reduced, high thermal budget requirement increases the cost of synthesis, thermal stresses developed damages the silicon wafer inconspicuously which significantly affects the device life time. In the case of CVD techniques, deposition of films can be performed at low temperature in comparison to thermal oxidation, but it cannot be operated at room temperature. Moreover the major disadvantage of this technique is the use of toxic, expensive reactant gases (silane, etc.) and complex system setup. Each and every process has its own advantages and disadvantages. Among these low temperature techniques, anodic oxidation is one which can be operated even below room temperature [7]. Numerous



research groups have investigated anodically grown oxide thin films for gate dielectric component in MOS devices [8, 10]. Anodic oxidation also known as anodization, it is an electrochemical process. It is a room temperature process and can be compatible with other processing sequences where redistribution of dopants is not desirable. Anodic oxidation is used in technology for the following several advantages such as it is a low temperature (even below room temperature) deposition technique, it provides very accurate control of the oxide thickness such that a complete reproducibility over the entire thickness is possible, with respect to the equipment investment it is a very low cost technique, creates no environmental pollution as this process does not involve any toxic gases. The present work is focused to investigate the effect of final voltage, current density and the amount of water on the growth rate, refractive index and the chemical composition of as-grown oxide thin films. The properties of the as-grown oxide films are studied using Ellipsometry, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM).

## **2. Experimental Procedure**

In the present work Czochralski (Cz) grown four inch diameter P-type boron doped (resistivity 1-10  $\Omega$ -cm) {100} oriented single side polished silicon wafers were used. The full wafer is diced into 23×23 mm<sup>2</sup> chip size for the deposition of oxide film using anodic oxidation technique. After dicing, chips are cleaned ultrasonically in acetone for 10 minutes followed by thorough rinse in deionized (DI) water. Aluminum is deposited on the rough surface side using DC sputtering for ohmic contact purpose. Solvent ethylene glycol is mixed with 0.04M potassium nitrate (KNO<sub>3</sub>) and different amounts of water served as electrolyte for the oxide growth. In two electrodes configuration, a customarily designed sample holder which provides gold contact to the sample is fixed as an anode and the platinum mesh is fixed as a cathode, the schematic of the experimental set up is as shown in Figure 1. The anode and cathode are separated by fixed distance of 1.5 cm and the pH of the solution is maintained as 4. The design of the chip holder is such that only 2.54 cm<sup>2</sup> circular area of the sample is exposed to the electrolyte solution. To remove the native oxide layer on the surface of the samples before just oxide deposition, samples are dipped in 1% hydrofluoric acid (HF) until wetting of the surface is ceased completely. The oxide growth is mainly dependent upon the water content in the electrolyte, processing parameters such as current density and temperature of electrolyte. To observe the effect of these parameters, oxide synthesis

is carried out in potentiodynamic mode with varying water content, current density and final voltage. At a fixed quantity of water (2.7 vol%) in the electrolyte the final voltage of the process is maintained as 200, 250 and 300 V in order to study the effect of final voltage on thickness of

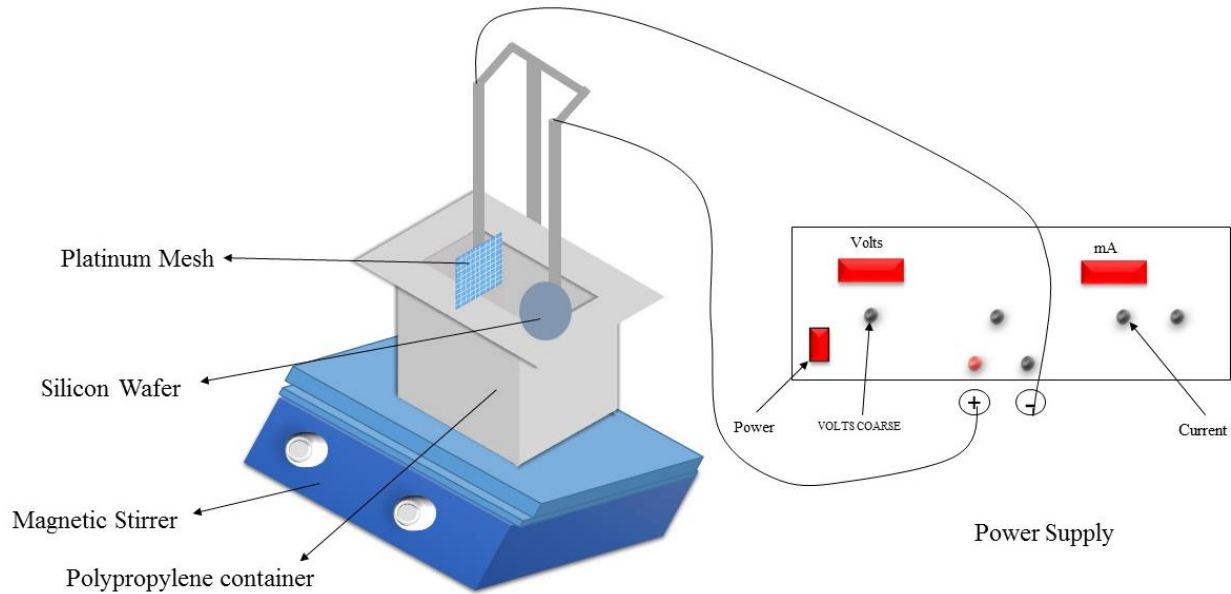


Fig. 1. Schematic diagram of Anodic Oxidation of silicon set-up.

the oxide. To investigate the effect of current density on film properties (especially effect on growth rate), at fixed quantity of water (2.7 vol%) in the electrolyte, the oxide growth is performed at three different current densities such as 5.5, 8, 10.5 mA/cm<sup>2</sup> with the final voltage of 300 V. In order to study the effect of amount of water added in the electrolyte on different properties of as-grown oxides films the water percentage in the electrolyte is varied as 2.7, 4.7, 6.7 and 10.7 vol% and the oxide synthesis is performed at 8 mA/cm<sup>2</sup> current density. After oxidation, the oxide samples are thoroughly cleaned in DI water to get rid of the absorbed glycol solvent. Ellipsometry (J.A. Woolam, model: M-2000D) measurements are performed to determine thickness and refractive index of the oxide films in the wavelength region of 193-1000 nm. FTIR (Bruker, TENSOR 37) is employed to evaluate the chemical bonds present in the oxide films. Scanning Electron Microscope (ZEISS, model: SUPRA40) is employed to study the morphology of the oxide films.

### 3. Results and Discussions

#### 3.1 Growth Characteristics

In order to study the effect of current density and electrolyte composition on growth rate of the oxide the oxide synthesis is performed in potentiodynamic regime with varying water percentage in the electrolyte, current density and final voltage (predetermined voltage).

In potentiodynamic mode, oxide synthesis is performed at fixed i.e. 2.7 vol% of water with varying current density (5.5, 8, and 10.5 mA/cm<sup>2</sup>) to elucidate the effect of current density on growth rate of the oxide. In the oxide synthesis the oxide growth is carried out at fixed current density (galvanostatic mode) up to the final voltage reaches the predetermined voltage of 300 V, thereafter the process is continued at 300 V (Potentiostatic mode) for 15 minutes. The variation in cell voltage during oxide deposition is recorded for every 1 minute of time and a graph is plotted between anodization time and the cell voltage which is as shown in Figure 2(a).

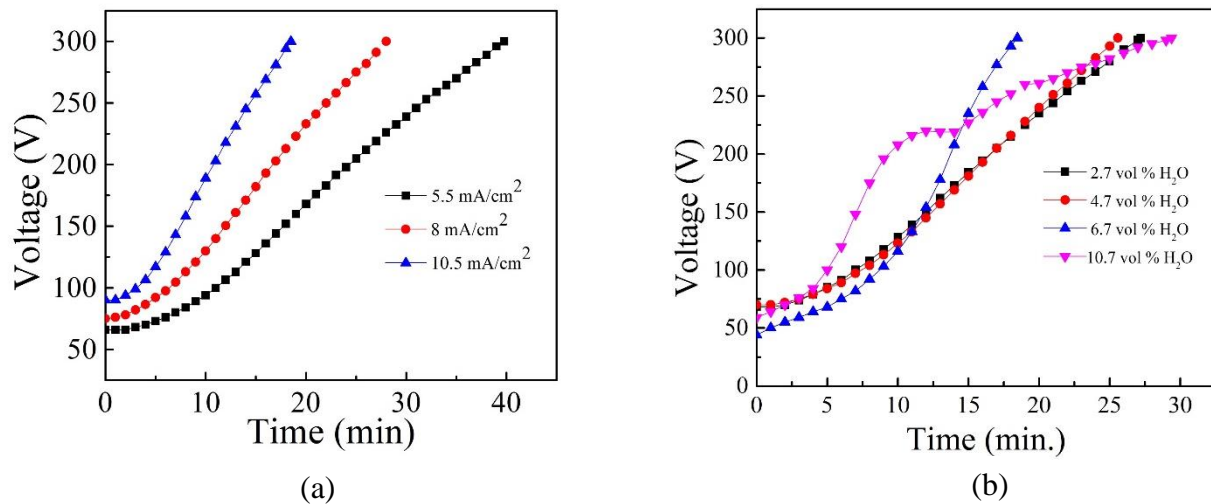


Fig. 2. Variation of voltage with time in potentiodynamic mode (a) at different current densities, 2.7 vol% of H<sub>2</sub>O (b) at different vol% of H<sub>2</sub>O, 8 mA/cm<sup>2</sup>.

From the figure we can observe that the voltage increases in order to maintain the same current density throughout the galvanostatic process. It can be observed from the Figure 2(a) that the voltage vs time behavior is same for all current densities. Also from the Figure 2(a) one can observe the role of current density on oxide growth, for instance the time required to attain the

predetermined voltage i.e. 300 V at 10.5 mA/cm<sup>2</sup> is shorter than that needed at 8, 5.5 mA/cm<sup>2</sup>. The time required to attain the 300 V is decreasing with increase in current density, also larger slope of the curves at higher current densities indicates faster growth rate which is attributed to enhanced diffusion rate of oxygenic ions [11]. Figure 2(b), shows the voltage vs time behavior of the oxides grown at fixed current density 8 mA/cm<sup>2</sup>, with varying amount of water in the electrolyte. In the Figure 2(b) the curves elucidates that the oxide growth behavior is different at different water percentages in the electrolyte. At 10.7 vol% of water the growth behavior is complex compare to the lower water percentages. From the figure it can be noticed that as water percentage increases from 2.7 to 6.7 vol% the growth rate is increasing, but again it decreasing at 10.7 vol% of water. At low water contents i.e. 2.7, 4.7 vol% initially voltage increases slowly, after 5 minutes the curves seems almost linear i.e. voltage increases linearly with time up to the predetermined voltage of 300 V indicating uniform oxide film. In case of 6.7 vol% of water the voltage rises slowly in the beginning of the oxidation but after 10-12 minutes of time it increases rapidly, moreover the time to reach 300 V and slope of the curve indicates very high growth rate of the oxide. The larger growth rate is due to the small resistance for the transfer of oxygenic species (OH<sup>-</sup> / O<sub>2</sub><sup>-</sup>) from the electrolyte into the anodic oxide film. At 10.7 vol% of water in the electrolyte, voltage rises abruptly after 5 min followed by a sudden decrease and there after voltage increases slowly up to the predetermined voltage (300 V). The abrupt change in the peak after 15 min probably designates structural and compositional changes in the oxide film.

### **3.2 Ellipsometry Study**

Ellipsometry study is performed to determine the thickness and refractive index of the films deposited under different conditions.

#### **3.2.1 Thickness**

Thickness of oxide films grown under different conditions is measured by using spectroscopic ellipsometry. Thickness of the oxides prepared at 2.7 vol% of water in the electrolyte and at three different current densities ranges around 155 nm. Thickness does not vary significantly with applied current density because the oxide growth employed here is based on the predetermined voltage but not on the fixed time period basis, and moreover the predetermined voltage (300 V) is same in all three depositions thus no significant variation in thickness with current density is obtained.

In order to investigate the uniformity in thickness of the as-grown oxide films thickness measurement using ellipsometry is performed at 4 different spots on the oxide surface.

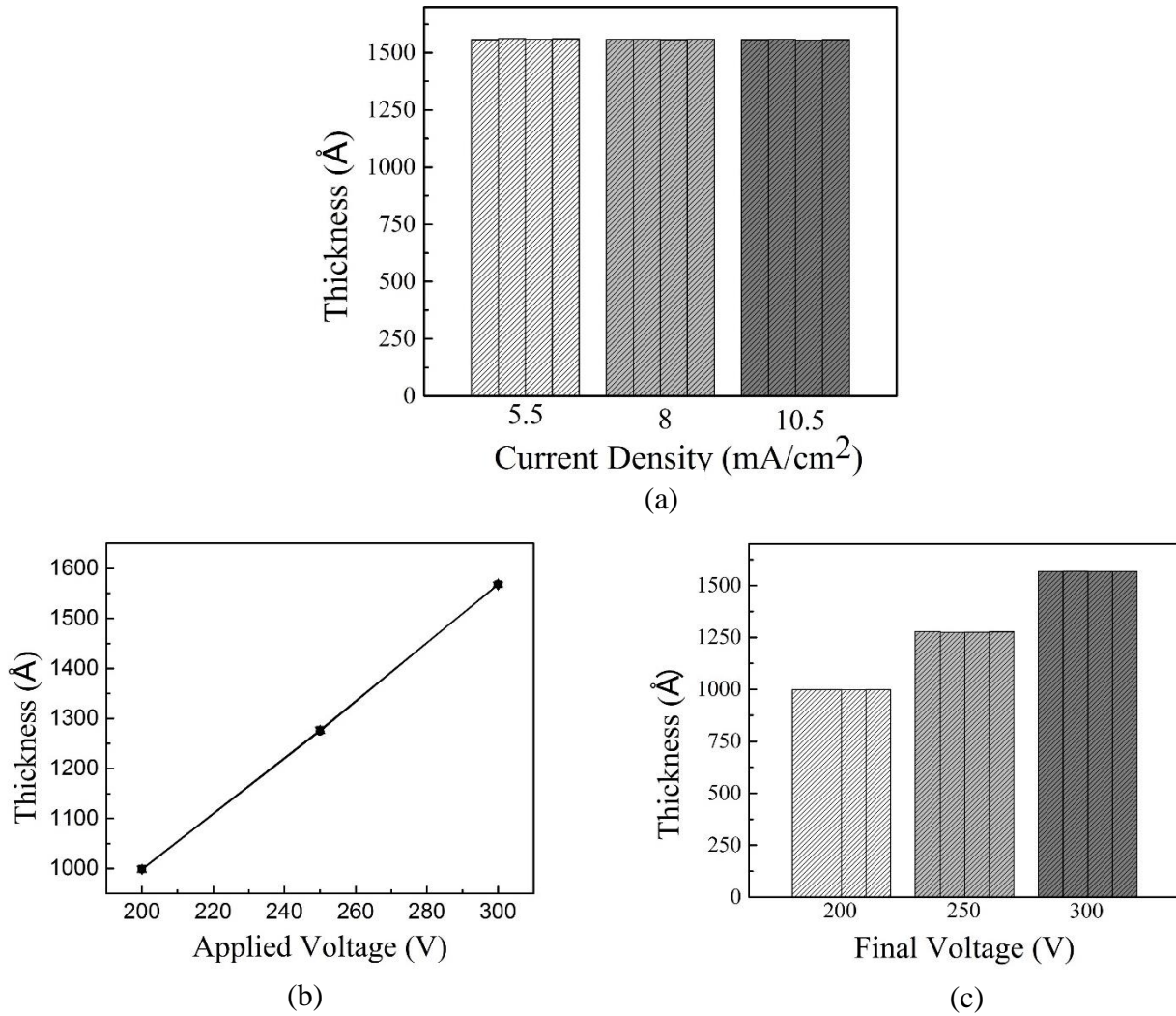


Fig. 3. (a) Thickness uniformity check by measuring film thickness at four different spots for the films grown in potentiodynamic mode at different current densities, 2.7 vol% H<sub>2</sub>O (b) effect of final voltage on thickness at 2.7 vol% H<sub>2</sub>O, 8 mA/cm<sup>2</sup> (c) thickness uniformity check at different final voltages, 2.7 vol% H<sub>2</sub>O, 8 mA/cm<sup>2</sup>.

The Figure 3(a) presents the comparison of film thicknesses measured at four different spots, from the figure the observed thickness variation of below 5 Å indicates that the films are uniformly grown on the silicon substrate. In order to study the effect of final voltage on thickness of the oxide films in potentiodynamic mode, oxide films are deposited at three different final voltages (200 V, 250 V, 300 V) at 8 mA/cm<sup>2</sup> fixed current density, 2.7 vol% of water in the electrolyte. From the Figure 3(b) it can be observed that the thickness increases linearly with final voltage. The Figure 3(c), shows the thickness uniformity of the films developed at different final voltages, from the graph the thickness variation of below (5Å) evident that the films have good thickness uniformity. Table 1 displays the oxide thickness and interfacial layer thickness at Si/SiO<sub>2</sub> for different amounts of water in the electrolyte. Oxide thickness increases with amount of water in the electrolyte maximum thickness of around 1 μm is obtained at 10.7 vol% of water. Similarly the amount of water also effects the interfacial layer at Si/SiO<sub>2</sub>, thickness of interfacial layer increases as water content in the electrolyte increases indicating increase in the roughness of interface layer at higher water percentages, this increase in roughness is due to the high growth rate of the oxide as water content in the electrolyte increases.

Table 1: Effect of water content in the electrolyte on oxide thickness, interfacial layer thickness (Si/SiO<sub>2</sub>) at 8 mA/cm<sup>2</sup> current density.

Regime: Potentiodynamic, pH=4, Current Density = 8 mA/cm <sup>2</sup>		
Water content (vol%)	Thickness of SiO <sub>2</sub> (nm)	Thickness of Interfacial Layer at Si and SiO <sub>2</sub> interface (nm)
2.7	156	0.32
4.7	165.6	6.02
6.7	164.8	7.44
10.7	≈1μm	-

### 3.2.2 Refractive Index

Refractive index of oxide films is determined by using variable angle Ellipsometry at 632.8 nm. Table 2 presents the refractive index of the films grown in potentiodynamic mode at 2.7 vol% of water in the electrolyte, 8 mA/cm<sup>2</sup> current density with varying final voltages. From the Table 2 it can be noticed that there is no significant change in the refractive index as the final voltage increased from 200 V to 300 V, however it increases slightly from 1.474 to 1.475.

Table 2: Effect of final voltage on refractive index of oxide films prepared at 2.7 vol% H<sub>2</sub>O, 8 mA/cm<sup>2</sup> in potentiodynamic mode.

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Regime: Potentiodynamic, pH=4, Water Content = 2.7 vol%

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Final voltage (V)	Refractive Index (n)
200	1.474
250	1.475
300	1.475

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Table 3: Effect of current density on refractive index of oxide films prepared in potentiodynamic mode at 2.7 vol% of water in electrolyte solution.

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Regime: Potentiodynamic, pH=4, Water Content= 2.7 vol%

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Current Density (mA/cm <sup>2</sup> )	Refractive Index (n)
5.5	1.475
8.0	1.475
10.5	1.474

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Table 3 presents the refractive indexes of the oxide films grown at 2.7 vol% of water with varying current densities. From the Table 3 it can be observed that the refractive index ranges around 1.474-1.475 when the applied current density is varied and keeping all other parameters fixed. The refractive index of anodically grown oxide films (1.47) developed in different operating conditions is slightly more than the thermally grown oxides (1.46), which is may be due to the higher density or more silicon content of the anodic oxide films. Table 4 presents the refractive index of the oxide films grown at 8 mA/cm<sup>2</sup>, with varying water content in the electrolyte. From the table it can be noticed that as water percentage increases the refractive index of the oxides decreases, it is due to the lower density/porosity and increasing number of Si-OH bonds [12-14] in the film as water percentage increases.

Table 4: Effect of water content on refractive index of oxide films prepared under potentiodynamic mode at 8 mA/cm<sup>2</sup>.

Regime: Potentiodynamic, pH=4, Current Density = 8 mA/cm <sup>2</sup>	
Water content (vol%)	Refractive Index (n)
2.7	1.475
4.7	1.44
6.7	1.437

### 3.3 Fourier Transform Infrared Spectroscopy (FTIR) Characterization

The FTIR spectra of the as-grown oxide films is recorded in the wave number range 400 – 4000 cm<sup>-1</sup> using BRUKER TENSOR 37 (resolution 4 cm<sup>-1</sup>) for finding the nature of chemical bonds and composition of the as-grown oxide films. The three characteristic vibrational modes exhibited by SiO<sub>2</sub> are namely rocking, bending and asymmetric stretching corresponding to 450 cm<sup>-1</sup>, 800 cm<sup>-1</sup> and 1075 cm<sup>-1</sup> [15]. The shift in the position of Si-O-Si asymmetric stretching peak occurs due to alteration in oxide thickness, stress/strain, porosity and the O/Si ratio of the oxide films [16-20].



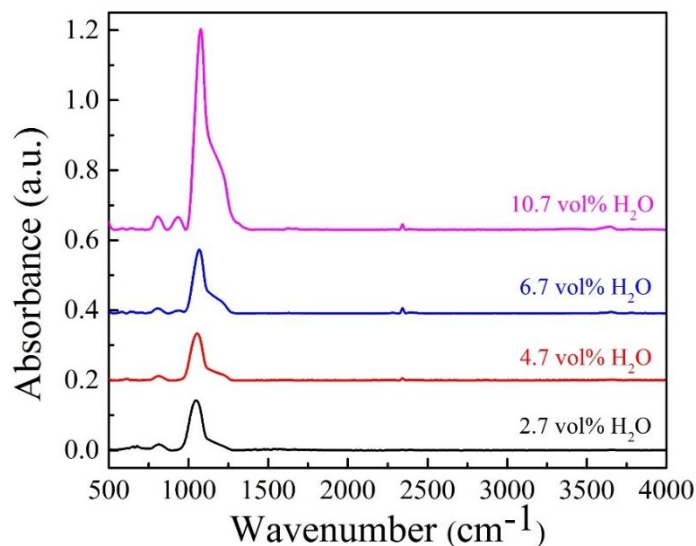


Fig. 4. FTIR absorption spectra of oxide films prepared at 8 mA/cm<sup>2</sup> current density with varying water percentage in the electrolyte solution.

Figure 4 shows the typical comparison FTIR absorption spectra of the oxide films prepared at 8 mA/cm<sup>2</sup> current density, varying water percentages (2.7, 4.7, 6.7, 10.7 vol% of water) in the electrolyte. The characteristic vibration modes of SiO<sub>2</sub> observed in the as-grown anodic silicon dioxide films are rocking (446-454 cm<sup>-1</sup>), bending (807 – 815 cm<sup>-1</sup>) and asymmetric stretching (1050 – 1077 cm<sup>-1</sup>) with asymmetric stretching peak as intense peak in all the samples. It can be observed from the figure that as the water percentage in the electrolyte increases from 2.7 to 10.7 vol% the position of asymmetric stretching peak shifting towards higher frequency i.e. from 1050 – 1077 cm<sup>-1</sup>. This increase in frequency of asymmetric stretching mode could be due to the structural and compositional changes [21, 22] in the film as the composition of the electrolyte is altered by changing the water percentage in the electrolyte. Apart from the characteristic vibration modes, peaks around 940 cm<sup>-1</sup> [23], 3400 cm<sup>-1</sup> & 3650 cm<sup>-1</sup> [24, 25] corresponds to the hydroxyl groups (OH) are observed in the films prepared with 6.7, 10.7 vol% of water in the electrolyte, which indicates incorporation of OH groups in the films as the water content in the electrolyte is increased. In case of the oxide film deposited with 10.7 vol% of water in electrolyte the increase in intensity of the 1077 cm<sup>-1</sup> peak is due to the higher thickness of the film, also the shoulder present at around 1200 cm<sup>-1</sup> [26, 27] reveals the existence of porosity in the film.

### 3.4 Surface Morphology Investigation

Surface morphology of the as-grown oxide films is investigated using SEM. Figure 5(a) & 5(b) shows the surface morphology of the oxide film developed at 2.7 vol% of water, two different

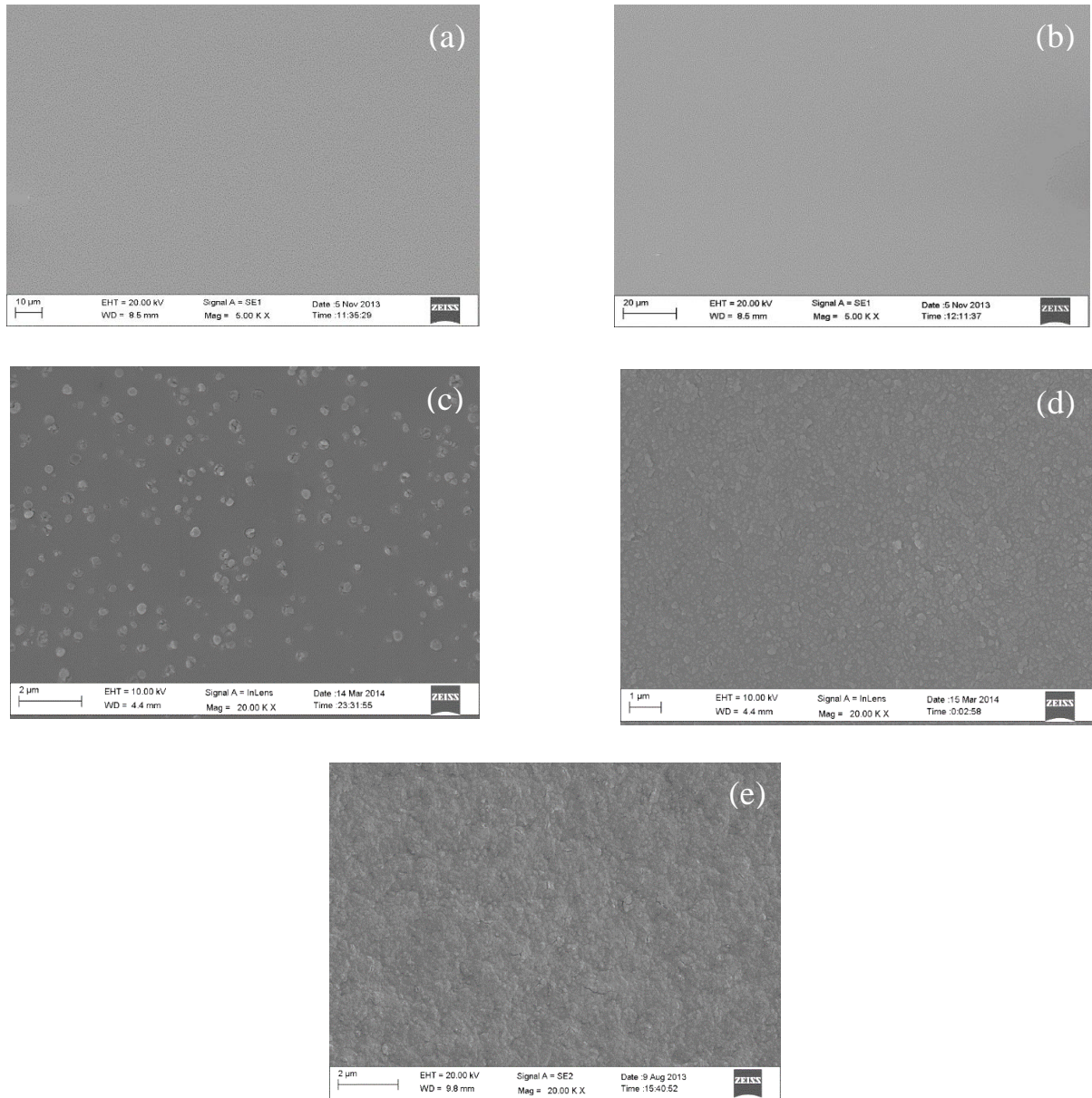


Fig. 5. Surface micrographs of the as-grown oxide films developed at 2.7 vol% of water (a) 5.5 (b) 8 mA/cm<sup>2</sup> (c) film developed at 4.7 vol% of water, (d) film developed at 6.7 vol% of water (e) film developed at 10.7 vol% of water, 8 mA/cm<sup>2</sup>.

current densities i.e. 5.5 and 8 mA/cm<sup>2</sup>. From the SEM images it can be observed that the oxide films does not show any nodular and agglomerated kind of features, rather shows uniform and non-porous film.

Figure 5 (c), (d) & (e) shows the surface micrographs of the as-grown oxide films developed at 4.7, 6.7 and 10.7 vol% of water, 8 mA/cm<sup>2</sup> current density. As the water percentage increases, at 4.7 vol% the oxide surface is partially covered by round spots of increased film thickness in the oxide, at 6.7 & 10.7 vol% of water the total oxide surface is covered by the oxide thickenings thus leads to thick oxide film at larger water contents in the electrolyte [28]. As it can be observed from the micrographs that the oxide surface becomes non uniform and rough as water percentage in the electrolyte is increased, it is also manifested from the high growth rate of the oxide at large water percentages discussed in the section 3.1.

#### **4 Conclusions**

Silicon dioxide thin films on silicon substrate are developed using anodic oxidation technique at room temperature. In the present work oxide films are developed in potentiodynamic mode. At fixed composition of the electrolyte solution oxide growth rate is predominantly influenced by current density, growth rate enhances as current density increases, in the present range study at 10.5 mA/cm<sup>2</sup> maximum growth rate is observed. The growth rate of the oxide also depends on composition of the electrolyte in particular on volume percentage of water in the electrolyte, growth rate increases with water content in the electrolyte maximum growth rate is obtained at 6.7 vol% of water above of this the growth rate decreases. The oxides grown in the electrolyte containing low water content i.e. 2.7 vol% are smooth and uniform in thickness. The thickness of the oxide increases as water percentage increases. Refractive index of the oxides decreases with increase in water percentage indicating poor density of the films at higher water percentages. The oxide films prepared in the electrolyte containing higher water contents shows increased hydroxyl incorporation. The surface of the oxides become more rough and non-uniform as water content in the electrolyte is increased.

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**Figure 2:** Variation of voltage with time in potentiodynamic mode (a) at different current densities, 2.7 vol% of H<sub>2</sub>O (b) at different vol% of H<sub>2</sub>O, 8 mA/cm<sup>2</sup>.

**Figure 3:** (a) Thickness uniformity check by measuring film thickness at four different spots for the films grown in potentiodynamic mode at different current densities, 2.7 vol% H<sub>2</sub>O (b) effect of final voltage on thickness at 2.7 vol% H<sub>2</sub>O, 8 mA/cm<sup>2</sup> (c) thickness uniformity check at different final voltages, 2.7 vol% H<sub>2</sub>O, 8 mA/cm<sup>2</sup>.

**Figure 4:** FTIR absorption spectra of oxide films prepared at 8 mA/cm<sup>2</sup> current density with varying water percentage in the electrolyte solution.

**Figure 5:** Surface micrographs of the as-grown oxide films developed at 2.7 vol% of water (a) 5.5 (b) 8 mA/cm<sup>2</sup> (c) film developed at 4.7 vol% of water, (d) film developed at 6.7 vol% of water (e) film developed at 10.7 vol% of water, 8 mA/cm<sup>2</sup>.

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**Table 3:** Effect of current density on refractive index of oxide films prepared in potentiodynamic mode at 2.7 vol% of water in electrolyte solution.

**Table 4:** Effect of water content on refractive index of oxide films prepared under potentiodynamic mode at 8 mA/cm<sup>2</sup>.

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