Optical Characterization of Anodically grown Silicon Dioxide Thin Films

Ashok Akarapu*, Prem Pal
MEMS and Micro/Nano systems Laboratory, Department of Physics, IIT Hyderabad, India
*Author for correspondence: ph11p1001@iith.ac.in

***Abstract*— In silicon-based fabrication processes, silicon dioxide (SiO_2) thin film is most widely used insulating film in the manufacture of integrated/discrete devices and microelectro-mechanical systems (MEMS). Various techniques have been established for the synthesis of silicon dioxide thin films. However, anodic oxidation method offers key advantages over the high temperature processes such as low cost, simple experimental set-up, low temperature, etc. In the present work SiO_2 thin films are developed on silicon using anodic oxidation technique at room temperature. Constant voltage mode is employed in order to investigate the effect of applied voltage and the electrolyte stirring on thickness, refractive index and chemical bonds of the as-grown oxide films. Spectroscopic ellipsometry and Fourier transform infrared spectroscopy (FTIR) are employed to characterize various properties of the as-grown oxide films. At the applied voltage of 250 V, the highest thickness of 134 nm is obtained. The oxides developed at higher voltages are slightly silicon rich. The present study is aimed to explore the applications of silicon anodic oxidation in MEMS/Microelectronics fabrication.**

***Index Terms*— Silicon dioxide, Anodic oxidation, Thin film.**

I. INTRODUCTION

Anodic oxidation technique is commonly used to generate oxides of metals (Al, Ta, W, etc.) and their alloys for various applications [1, 2]. This technique offers many advantages over high temperature processes such as low cost, low thermal budget, simple experimental set-up and the control of oxide thickness by varying oxide growth parameters, etc. The low temperature characteristics of this technique is advantageous for the deposition of oxide layer on heat sensitive materials such as *a*-Si, SiGe alloy and 4H-SiC, etc. [3-5] and to avoid dopant redistribution during deposition process.
Silicon dioxide (SiO_2) thin films are extensively used as gate dielectric in MOS transistors, passivation of silicon devices, isolation, as mask against diffusion & implantation of dopants and also in microelectromechanical systems (MEMS) [6], etc. Several growth and deposition based techniques have been established for creating silicon dioxide thin films. Thermal oxidation process is known to provide good quality SiO_2 films hence extensively used for synthesis of gate dielectrics in MOS transistors.
The thickness of the oxide needs to be thin as the device dimensions continue to shrink in order to obtain higher packing density for better performance. Anodic oxidation technique is advantageous in this perspective as the oxide thickness can easily controlled by varying growth parameters. Numerous research groups have been investigated the anodically grown SiO_2 thin films for the application of gate dielectric in MOS transistors [7-9]. The applications of these anodically grown SiO_2 films could be tested in other semiconductor fields where the thickness, density and the composition, etc. may be important considerations. In this view point, it is important to understand the effect of various growth parameters and composition of the electrolyte solution on different properties of as-grown oxide films as these factors significantly affect the quality of the deposited films. The present study aims to investigate the effect of voltage and the electrolyte stirring on various properties of as-grown oxide films developed in constant voltage (potentiostatic) mode of growth.

II. EXPERIMENTAL DETAILS

Czochralski (Cz) grown four inch P-type boron doped (resistivity 1-10 Ωcm) {100} oriented single side polished silicon wafers were cut into 23×23 mm^2 chip sizes for SiO_2 growth by anodic oxidation. Aluminum is deposited on rough surface of the sample using e-beam evaporation technique for ohmic contact purpose. After dicing, substrates were ultrasonically cleaned sequentially in acetone and deionized (DI) water for 10 minutes respectively. Finally the substrates were thoroughly rinsed in DI water and dried with compressed air. Ethylene glycol solvent (purity> 99%, Sigma Aldrich) mixed with 0.04M KNO_3 and fixed quantity (0.5 vol%) of water served as electrolyte solution for oxide growth of all the samples.
All oxide films are developed at room temperature with pH of the solution is maintained as three. In the Parallel plate two electrode configurations a specially designed sample holder which provides gold contact to the silicon substrate is fixed as anode and the platinum mesh as cathode. Both the electrodes are separated by fixed distance of 2 cm. For the oxide growth constant potential (potentiostatic) regime is employed, in which power supply is turned off as soon as the total current fall down to a minimum current of 2 mA. In order to investigate the effect of stirring on oxide film characteristics, the deposition is carried out with and without stirring of electrolyte.
Prior to oxidation, in order to etch out native oxide layer the samples were dipped in 1% hydrofluoric acid (HF) solution until wetting of the sample surface is ceased. Then after the samples are thoroughly rinsed in DI water to ensure that no traces of HF being left on the sample. After oxidation, the samples are thoroughly cleaned in DI water to get rid of the adsorbed glycol solvents. Ellipsometric (model: M-2000D, J.A. Woollam, USA) measurements at three incidence angles (65º, 70º and 75º) were performed to measure thickness and refractive index of the as-deposited oxide films. FTIR (Bruker, model: ALPHA) measurement in ATR module is

V. K. Jain and A. Verma (eds.), *Physics of Semiconductor Devices*, Environmental Science and Engineering,
DOI: 10.1007/978-3-319-03002-9_109, © Springer International Publishing Switzerland 2014

performed to investigate the nature of chemical bonds in the as-grown oxide films.

III. RESULTS & DISCUSSIONS

3.1 Current density dependence on oxidation time

In potentiostatic mode, during oxide growth the fall in current is recorded every minute at each specific applied voltage and a graph is plotted between oxidation time and the current density for various applied voltages. The Fig.1 shows the variation in current density with oxidation time at voltages 50-250 V. The shape of the curve suggests that the oxide growth is parabolic at voltages greater than 50 V.

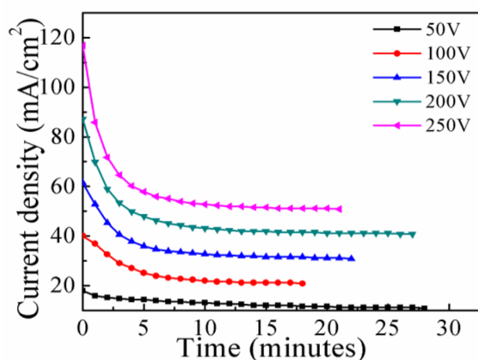

FIG.1. Variation in current density with oxidation time at various voltages (50-250 V).

From the graph it can be observed that the initial current density increases with the applied voltage. It can also noticed from the figure that current decreases rapidly in the initial 4 minutes of oxidation and the decrease become more rapid with rise in impressed voltage indicating faster growth rate of the oxide in the initial stage of oxidation. After initial rapid decrease, the current density is almost saturating or it decreases very slowly. In this stage the oxide growth rate decreases, owing to the reduction in the diffusion of oxygenic ions which happens due to fall in the electric field [10, 11].

3.2 Ellipsometric study of Thickness and Refractive index

Spectroscopic Ellipsometry is non-destructive, contactless and allows quick measurement, hence this technique is widely used to determine thickness and optical constants such as refractive index (n), extinction coefficient (k) of thin films [12]. Various properties of oxide films are characterized using Ellipsometric measurements which are presented in the following section.

3.2.1 Thickness

Ellipsometry is employed to determine the thickness of as-grown oxide films at three incidence angle (65º, 70º and 75º) of light. In order to evaluate the uniformity of the oxide films prepared at various voltages (50–250 V), thickness is measured at different spots and the comparison of the same is shown in Fig.2. From Fig.2 it can be observed that the thickness variation of 1-5 Å at all applied voltages indicates that the as-grown films are uniform in thickness.

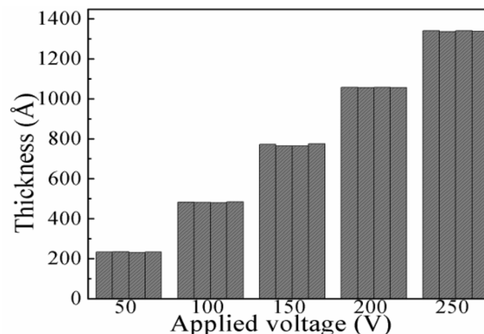

FIG.2. Thickness of oxide films measured at four different spots to investigate the uniformity in thickness at 50-250 V.

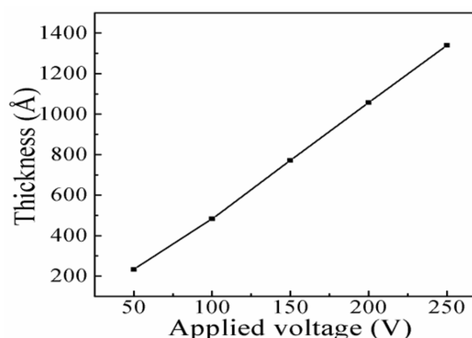

FIG.3. Thickness of oxides as function of applied voltage.

The Fig.3 above shows the effect of applied voltage on thickness of oxide films developed at 50-250 V. It can be noticed from the graph that the thickness increases linearly with applied voltage. Since increase in voltage enhances the driving force of the transport of oxygenic ions through the oxide layer for the growth of the oxide to proceed at Si/SiO_2 interface [10, 11]. The slope of the straight line indicates that the growth rate of the oxide proceeds at 5.25 Å/V. Similarly Y intercept gives the native oxide thickness which is zero in the present experiment.

3.2.2 Refractive index

Refractive index of oxide films is determined by using variable angle Ellipsometry at the fixed wavelength of 632.8 nm. Table 1 displays the refractive index of the oxide films prepared with and without mechanical stirring of the electrolyte. Usually refractive index of the silicon dioxide films is function of composition or stoichiometry [13-15] and density/porosity of the films [16-18].
In Table 1 it can be observed that the refractive index of the oxides increases from 1.45 to 1.478 as applied voltage increased from 50 to 250 V with the increment of 50 V. Oxides prepared above 50 V have slightly larger refractive index than thermally grown silicon oxide. It may be due to more silicon content in the oxide films [14, 19]. Higher silicon content in oxide films is confirmed by FTIR measurement results, which are presented in the next section, where the

small intense peaks of oxygen deficiency i.e. Si-Si bond at 653-670 $cm^{-1}$and sub oxides around 988-1000 $cm^{-1}$are observed [20,21].

TABLE 1. Refractive index of the oxide films prepared in Potentiostatic mode with and without mechanical stirring of the electrolyte solution

Regime: Potentiostatic, pH=3, Water content = 0.5 vol%	
Applied Voltage (V)	Refractive Index (n) (with/without stirring)
50	1.45
100	1.470/1.466
150	1.473
200	1.475
250	1.478/1.474

3.2 Fourier Transform Infrared Spectroscopy (FTIR) study

FTIR in ATR module with 45° of light incidence is employed for the frequency range of 550-4000 cm^{-1} in order to determine the nature of chemical bonds in the as-grown SiO_2 thin films. Fig.4 shows the FTIR absorption spectra of the films developed at various voltages.

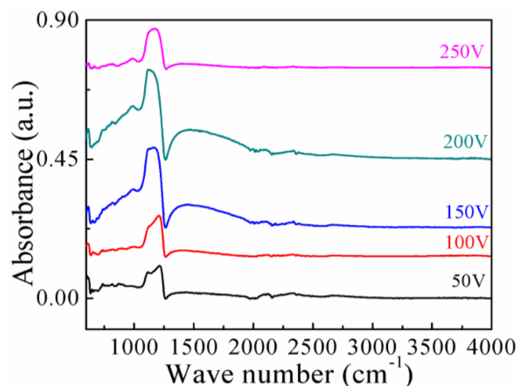

FIG.4. FTIR absorption spectra of oxide films developed at 50-250V.

Two principal absorption peaks which are characteristic vibrations of Si-O-Si are observed in the wave number range (817-821 cm^{-1}) and (1121-1213 cm^{-1}). These peaks corresponds to Si-O bending and Si-O-Si asymmetric stretch vibrations respectively [20, 22, 23]. Shift in the position of Si-O-Si asymmetric stretching peak is ascribed to several factors such as alteration in oxide thickness, stress/strain, porosity and the O/Si ratio of the oxide films [14, 17, 24-26].
It can be observed from the FTIR spectra shown in Fig.4 that the position of Si-O-Si asymmetric stretching peak is shifting with applied voltage. The reason is that applied voltage influences the growth rate, which in turn affects the structure and stoichiometry of the oxides that results in the shifting of Si-O-Si asymmetric stretching peak position. In addition to two characteristic Si-O vibrational peaks, weak intense peaks corresponding to oxygen vacancies around (653-678 cm^{-1}, Si-Si bond) [20], carbon impurity (1400-1500 cm^{-1}) [27], Si-H (2100-2300 cm^{-1}) [28] and silicon suboxide species (SiO_x, x~0.5) in the frequency range of 988-1000 cm^{-1} [21] are also observed in the spectrum. The absence of the peaks corresponding to Si-OH at 940 cm^{-1} [29] and H-O-H vibrations bending at 1620 cm^{-1}, stretching at 3640 cm^{-1} [29] in the spectra confirms the absence of water and hydroxyl ions in the deposited oxide films.

3.3 Effect of electrolyte stirring on various properties of SiO_2

In order to find the effect of electrolyte stirring on thickness and other properties of as-prepared oxide films, oxide synthesis is carried out with and without mechanical stirring of electrolyte at 100 and 250 V.

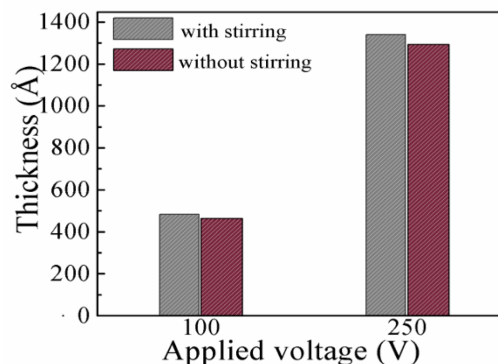

FIG.5. Effect of mechanical stirring of the electrolyte on thickness of as-grown oxide films.

Fig.5 shows the comparison of oxide film thickness developed with and without stirring of electrolyte at 100 & 250 V. The thickness of the film deposited without stirring is about 4% smaller than that deposited with stirring of the electrolyte. The reduction in oxide thickness may be due to the lack of convective contribution in the absence of mechanical stirring to the total flux of anionic (OH^- or O_2^-) species as they are essential for the oxidation to take place at the anode (i.e. silicon) of the cell.

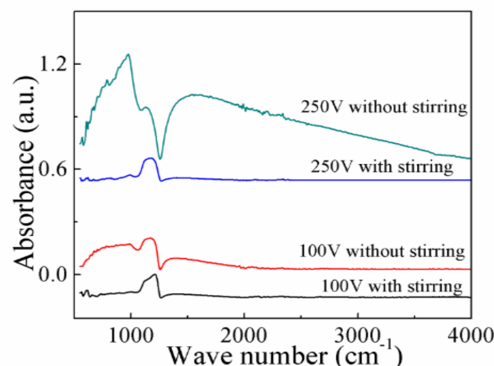

FIG.6. FTIR absorption spectra of oxide films deposited at 100 & 250 V with and without mechanical stirring of electrolyte.

Fig.6 shows the comparison of FTIR absorption spectra of oxides grown with and without mechanical stirring of electrolyte at 100 and 250 V. It can be visualized in the

spectra that the shape and position of Si-O-Si asymmetric stretching peak varies in the two cases of oxidation. This variation may be attributed to the effect of mechanical agitation on the composition and structure of deposited oxides that leads to alteration in Si-O-Si bond angle [28-30] hence shift in the position of the Si-O-Si asymmetric stretching peak.

The stirring of the solution also affects the refractive index of the oxides as presented in Table 1. The refractive index of the films prepared without stirring of electrolyte at voltages 100 and 250 V is slightly smaller than the films formed with stirring of the solution. This decrease in refractive index is attributed to change in composition and the density of the oxides caused by absence of mechanical stirring of electrolyte.

IV. CONCLUSIONS

In conclusion, we have developed silicon dioxide thin films on silicon at various applied voltages using anodic oxidation technique at room temperature in constant voltage mode. The films are uniform in thickness, the measured uniformity is below 5 Å. In the constant voltage mode the applied voltage greatly influences the thickness and other properties of the oxides. A linear relation is obtained between the applied voltage (50-250 V) and the thickness of the as-grown oxides. The highest thickness of 134 nm is obtained at 250 V. Growth rate of 5.25 Å/V is obtained with 0.5 vol% of water added into the electrolyte. The Refractive index of the oxides developed above 100 V is slightly higher than the thermally grown oxides indicating that the films are silicon rich. The FTIR spectra of the oxides reveals the absence of water and hydroxyl ions incorporation in the films. Reduction in oxide thickness and differences in other properties of oxide films when compared with the results obtained by the stirring of electrolyte evidences the effect of absence of stirring on oxide growth. In the present study, it may be concluded that the applied voltage and the electrolyte stirring significantly influences the thickness and other characteristics of the oxide films.

V. REFERENCES

[1] G.E. Thompson, *Thin Solid Films,* 297, 192 (1997).

[2] V. Karastoyanov, M. Bojinov, *J Solid State Electrochem, 13, 309* (2009).

[3] H. Hasegawa, S. Arimoto, S. Nunjo, H. Yamamoto, H. Ohno, *J Electrochem Soc* 135, 424 (1988).

[4] J. Rappich, I. Sieber, A. Schopke , W. Foussel, M. Gluck, J. Hersener, *Mat Res Soc Symp Proc* 451, 215 (1997).

[5] W.S. Woon, S.D. Hutagalung, K.Y. Cheong, *Thin Solid Films* 517, 2808 (2009).

[6] V. Bhatt, S. Chandra, *J. Micromech. Microeng.* 17, 1066 (2007).

[7] T.F. Hung, H. Wong, Y.C. Cheng, C.K. Pun, *J. Electrochem. Soc.* 138, 3747 (1991).

[8] H. Aguas, A. Goncalves, L. Pereira, R. Silva, E. Fortunato, R. Martins, *Thin Solid Films,* 427, 345 (2003).

[9] W.B. Kim, T. Matsumoto, H. Kobayashi, *J. Appl. Phys.* 105, 103709 (2009).

[10] L. Sun, S. Zhang, X.W. Sun, H. Xiaodong, *Journal of Electroanalytical Chemistry*, 637, 6 (2009).

[11] Y.F. Mei, X.L. Wu, T. Qiu, X.F. Shao, G.G. Siu, Paul K. Chu, *Thin Solid Films,* 492, 66 (2005).

[12] B.M. Ayupov, S.F. Devyatova, V.G. Erkov, L.A. Semenova, *Russian Microelectronics*, 37, 141 (2008).

[13] M.F. Ceiler Jr., P.A. Kohl and S.A. Bidstrup, *J. Electrochem. Soc.* 142, 2067 (1995).

[14] C.F. Lin, W.T. Tseng, M.S. Feng, *J. Appl. Phys.* 87, 2808 (2000).

[15] T. Roschuk, J. Wojcik, X. Tan, J.A. Davies, P. Mascher, *J. Vac. Sci. Technol. A,* 22, 883 (2004).

[16] M. Stadtmueller, *J. Electrochem. Soc*. 139, 3669 (1992).

[17] G. Lucovsky, M.J. Manitini, J.K. Srivastava, E.A. Irene, *J. Vac. Sci. Technol. B,* 5, 530 (1987).

[18] B.N. Joshi, A.M. Mahajan, *Optoelectronics and Advanced Materials – Rapid Communications,* 1, 659 (2007).

[19] W.A. Pliskin, *J. Electrochem. Soc.* 134, 2819 (1987).

[20] M.I. Alayo, I. Pereyra, W.L. Scopel, M.C.A. Fantini, *Thin Solid Films,* 402, 154 (2002).

[21] J. Lambers, P. Hess, *J. Appl. Phys.* 94, 2937 (2003).

[22] F.L. Galeener, *Physical Review B,* 19, 4292 (1979).

[23] P.G. Pai, S.S. Chao, Y. Takagi, G. Lucovsky, *J. Vac. Sci. Technol. A,* 4, 689 (1986).

[24] W.A. Pliskin, H.S. Lehman, *J. Electrochem. Soc.* 112, 1013 (1965).

[25] W.A. Pliskin, *J. Vac. Sci. Technol.* 14, 1064 (1977).

[26] I.W. Boyd, J.I.B. Wilson, *Appl. Phys. Lett.* 50, 320 (1987).

[27] L.L. Tedder, J.E. Crowell, M.A. Logan, *J. Vac. Sci. Technol. A,* 9, 1002 (1991).

[28] D.V. Tsu, G. Lucovsky, B.N. Davidson, *Physical Review B,* 40, 1795 (1989).

[29] W.S. Liao, C.H. Lin and S.C. Lee, *Appl. Phys. Lett.* 65, 2229 (1994).

[30] D.J. Monk, D.S. Soane, R.T. Howe, *Transducers, juni* 24-27, 647 (1991).