

## INFLUENCE OF TITANIUM-TETRA-ISOPROPOXIDE FLOW ON TiO<sub>2</sub> DOPED SiO<sub>2</sub> FILMS FOR WAVEGUIDE APPLICATIONS

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The GeCl<sub>4</sub> and TiCl<sub>4</sub> are generally used for germanium and titanium doping into SiO<sub>2</sub> films for waveguide applications. Both GeCl<sub>4</sub> and TiCl<sub>4</sub> are metal halides and produce HCl as a byproduct during the deposition process which is highly toxic and corrosive in nature. Among the metalorganic precursors, titanium tetra-isopropoxide (TTIP) has been most widely used because of low carbon contamination in the deposited films and its high vapor pressure. In the present paper we present for the first time the TiO<sub>2</sub> doped SiO<sub>2</sub> films deposited by indigenously developed FHD system by using TTIP and Octamethylcyclotetrasiloxane (OMCTS) as a source material for TiO<sub>2</sub> and SiO<sub>2</sub> respectively. The effect of TTIP flow rate on the optical, structural and elemental properties of the deposited films have been studied. The refractive index and thickness of the deposited films is studied by ellipsometer. Scanning Electron Microscope (SEM) with EDAX attachment is used to study the surface morphology and elements of the deposited films. The XRD patterns of TiO<sub>2</sub> doped SiO<sub>2</sub> films shows two strong peak at  $2\theta = 38.3^\circ$  and  $2\theta = 44.6^\circ$  corresponding to the (004) anatase phase and (210) rutile phase of TiO<sub>2</sub>. The confirmation of TiO<sub>2</sub> doping is done by EDAX analysis.

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### 1. Introduction

Optical quality films of 10 – 20  $\mu\text{m}$  thickness are a basic requirement for integrated optics devices that are fabricated on silicon substrates. Numbers of specialized methods have been developed for them. These include wet thermal oxidation and thermal nitridation, sputtering, low pressure and plasma enhance chemical vapor deposition and flame hydrolysis. Each method has its own advantages and disadvantages. In CVD the process is time consuming and suffers from a limit in ultimate thickness. In case of PECVD the nature of the process gases makes the deposition system complicated and expensive. Sol-gel technology offers an alternative method of depositing glassy films based on the hydrolysis and polycondensation of metal alkoxides. Unfortunately the basic sol-gel process suffers from serious limitations when it comes to depositing thick, films, which is that the maximum thickness of a layer from a single deposition. Thicker layers generally crack as a result of shrinkage at the drying stage [1].

Flame Hydrolysis Deposition (FHD) technique is the most economical, simple and high growth rate technique for the deposition of high quality optical films. This method was originally developed for fiber preform fabrication. The silica waveguide can be formed on crystalline silicon substrates by a combination of FHD and Reactive Ion Etching (RIE) [2]. Their simple and clear core structures, low propagation loss and almost perfect field matching to optical fibers has lead to silica waveguides on silicon attracting increasing attention in recent years. A simple waveguide structure consists of three layers: buffer, core (guide), and cladding (cover cap). The light

confinement is done by increasing the refractive index of the core layer relative to the upper and lower cladding. This is accomplished by introduction of various dopants e.g., titanium or germanium to the gas mixture during deposition.

The  $\text{GeCl}_4$  is widely used for the germanium doping into  $\text{SiO}_2$  films [3-8]. This  $\text{SiO}_2$ - $\text{GeO}_2$  film have lower melting temperature and low propagation loss than  $\text{SiO}_2$ - $\text{TiO}_2$  films but careful attention has to be paid during the consolidation to prevent the  $\text{GeO}_2$  contents from vaporizing. The  $\text{TiCl}_4$  has been widely used in the deposition of  $\text{TiO}_2$  doped  $\text{SiO}_2$  films [2, 9-10]. Both  $\text{GeCl}_4$  and  $\text{TiCl}_4$  are metal halides and produce  $\text{HCl}$  as a byproduct [11-13] during the deposition process which is highly toxic and corrosive in nature. Among the metalorganic precursors, titanium tetraisopropoxide (TTIP) has been most widely used because of low carbon contamination in the deposited films and its high vapor pressure [14]. Though TTIP alone can produce  $\text{TiO}_2$  by thermal decomposition, oxygen source such as  $\text{O}_2$  and  $\text{N}_2\text{O}$  are added along with TTIP to improve film quality. Hence, in this present study we have used TTIP as precursor for doping of  $\text{TiO}_2$  in  $\text{SiO}_2$  films. Generally  $\text{SiO}_2$  films are deposited by the hydrolysis of  $\text{SiCl}_4$  in a high temperature  $\text{H}_2$ - $\text{O}_2$  flame. In this present paper we have replaced the commonly used  $\text{SiCl}_4$  by organic compound Octamethylcyclotetrasiloxane (OMCTS). This liquid precursor has low vapor pressure, non corrosive nature, low toxicity and safer to handle as compare to  $\text{SiCl}_4$ . In the second section of the paper the experimental setup and processing parameters have been discussed. The results are discussed in the third section of the paper. The fourth section concludes the paper.

## 2. Experimental:

Figure 1 shows the schematic of the experimental setup used in the present study. The system has been developed indigenously at Department of electronics. Silicon wafers (p-100) used as substrate, were cleaned by Trichloroethylene, Acetone and Methanol for removal of contaminations.

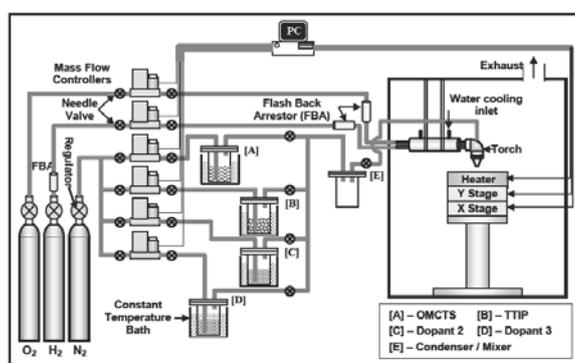


Fig. 1. Schematic of the experimental set of Flame Hydrolysis Deposition system.

The FHD system was powered ON and the MFC were allowed to heat up for better performance. After some time the MFC of hydrogen and oxygen were set at 2.0 SLPM and 0.6 SLPM. Substrate temperature was kept constant at  $700^\circ\text{C}$  throughout deposition processes. The flame was ignited at the nozzle end and allowed to get stable. Then the flow rate of precursor OMCTS (carrier gas nitrogen) was set to 0.2 SLPM and kept constant through out the processes. In this study the flow of TTIP (carrier gas nitrogen) was varied from 0.04 – 0.10 SLPM with a step of 0.02 SLPM. Both the precursors were passed through the condenser/mixer ([E] as shown in figure 1) for good mixing and then injected at the center of the flame. The deposition time for all the processes is 1.5 min. The effects of the flow rate of TTIP (carrier gas nitrogen) on refractive index, thickness, surface and percentage of elements were studied.

### 3. Results and discussion

The effect of TTIP (carrier gas N<sub>2</sub>) flow rate on refractive index and thickness of the deposited TiO<sub>2</sub> doped SiO<sub>2</sub> film have been studied using Philips SD-1000 Ellipsometer at 632.8 nm wavelength. The measured values of refractive index have been presented graphically in Figure 2. It is clearly observed from the Figure 2 that refractive index of deposited TiO<sub>2</sub> doped SiO<sub>2</sub> films increases with corresponding increase in TTIP flow rate. This increase in refractive index is due to the increase in TiO<sub>2</sub> contents in deposited films. This is evident from the EDAX studies (see Figure 5).

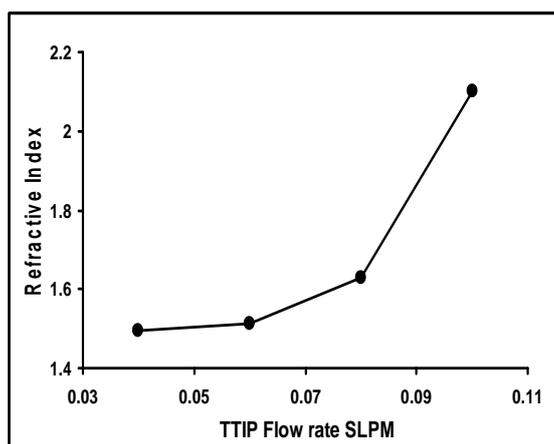


Fig. 2. Effect of TTIP flow rate on refractive index of TiO<sub>2</sub> doped SiO<sub>2</sub> films.

The effect of TTIP (carrier gas N<sub>2</sub>) flow rate on thickness of the deposited TiO<sub>2</sub> doped SiO<sub>2</sub> films have been presented graphically in Figure 3. From the figure it is depicted that the thickness of the deposited films increases with the corresponding increase in TTIP flow rate. The concentration of reactant species increases with corresponding increase in flow rate of TTIP which leads to increase in growth rate of the deposited film. Hence, we can conclude that the thickness of the film increases with corresponding increase in flow rate of TTIP. There is a difference of 150Å in thickness between the first and the last sample which is negligible for the waveguide application.

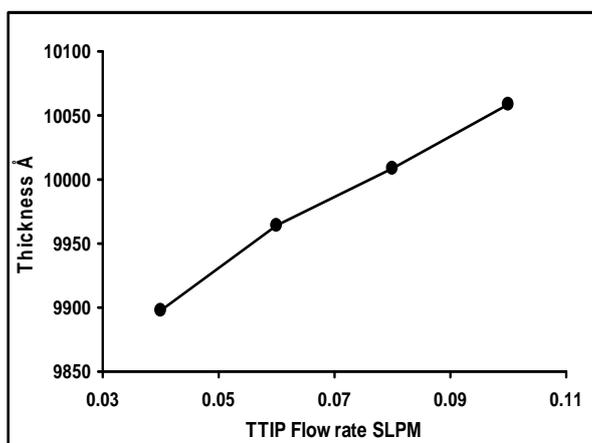


Fig. 3. Effect of TTIP flow rate on thickness of deposited TiO<sub>2</sub> doped SiO<sub>2</sub> films.

The surface morphology of the TiO<sub>2</sub>-doped SiO<sub>2</sub> films was studied using Scanning Electron Microscope (JEOL/EO make JSM-6360 model).

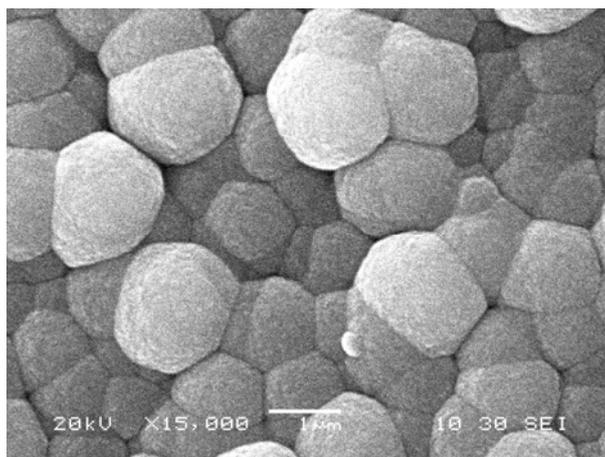


Fig. 4. SEM microphotograph of the sample DOMCTS-TTIP4.

Figure 4 illustrates the scanning electron microphotograph of a sample. It is depicted from the image that the film is crystalline in nature as compared to the SEM image of undoped  $\text{SiO}_2$  films [15]. The  $\text{SiO}_2$  :  $\text{TiO}_2$  particle sizes were found to be around  $1\mu\text{m}$ . This particle size is much greater than the films deposited by TEOS due to the high growth rate of the precursor OMCTS [16].

The elemental analysis of  $\text{TiO}_2$  doped  $\text{SiO}_2$  films were carried out using the EDAX technique. Figure 5 shows the plot of Oxygen and Titanium percentage in deposited films for TTIP flow variations. It is depicted from the figure that the Oxygen and Titanium counts decrease and increase respectively with corresponding increase in TTIP flow rate.

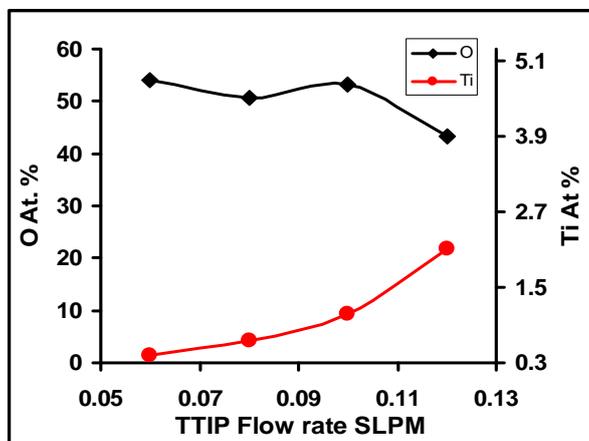


Fig. 5. Effect of TTIP flow rate on Oxygen and Titanium percent in deposited  $\text{TiO}_2$  doped  $\text{SiO}_2$  films.

The crystal analysis of deposited  $\text{TiO}_2$  doped  $\text{SiO}_2$  films have been carried out by X-ray diffraction technique (Bruker AXS D8 Advance Model). The XRD pattern of the  $\text{TiO}_2$  doped  $\text{SiO}_2$  films is as shown in Figure 6.

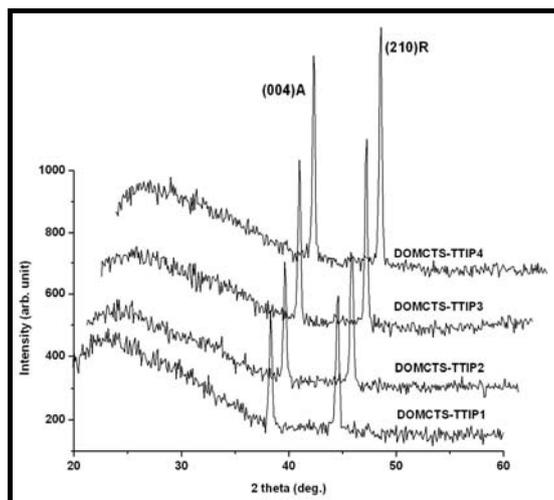


Fig. 6. XRD pattern of the TiO<sub>2</sub> doped SiO<sub>2</sub> films

It is depicted from the figure that two strong peak appears at  $2\theta = 38.3^\circ$  and  $2\theta = 44.6^\circ$  is due to the (004) anatase phase and (210) rutile phase of TiO<sub>2</sub>. The broad peak between  $2\theta = 20^\circ$ - $30^\circ$  corresponds to SiO<sub>2</sub> [17-20]. It is clearly observed from the figure that the peak intensities of both peaks increases with corresponding increase in TTIP flow rate. By comparing the XRD pattern of films the peak due to (210) rutile phase is dominant over (004) anatase phase.

#### 4. Conclusion

The TiO<sub>2</sub>-doped SiO<sub>2</sub> films have been successfully deposited using indigenously developed FHD system. The refractive index of the films increases with the increase of TTIP flow rate hence, we can conclude that the refractive index of the films can be controlled by the flow rate of TTIP. SEM microphotograph shows particle size of around 1  $\mu\text{m}$ . The size of the particle can be controlled by the flow of the precursors. EDAX study confirms the doping of TiO<sub>2</sub> in the SiO<sub>2</sub> films. No chlorine contains and other impurities are observed in the deposited films. In the present study the deposited films were found to be clear and transparent instead of white fluffy, which is the nature of the FHD films. The characterizations were carried out on As-deposited films. However, the effect of annealing on the properties of the films can be the further scope of study. The deposited films not only have applications in the field of waveguides but are also useful in the industrial waste water treatment and solar cells.

#### References

- [1] A. S. Holmes, R. R. A. Syms, Ming Li, Mino Green, *Applied optics* **32**(25), 4916 (1993).
- [2] Masao Kawachi, *Optical and Quantum Electronics*, **22**, 391 (1990).
- [3] Dongwook Shin, *J. Ceramic Processing Research* **7**(4), 379 (2006).
- [4] Pushkar Tandon and Heather Boek, *J. of Non-Crystalline Solids*, **317**, 275 (2003).
- [5] Jesus M. Ruano, Vincent Benoit, J. Stewart Aitchison and Jonathan Cooper, *Annal Chem.* **72**, 1093 (2000).
- [6] Dongwook Shin, and Jae-HO Eo, *J. Ceramic Processing Research*, **6**(4), 345 (2005).
- [7] G. Barbarossa, P. J. R. Laybourn, *Electronics Letters*, **28**(5), 437 (1992).
- [8] A. J. McLaughlin, J. R. Bonar, M. G. Jubber, P. V. S. Marques, S. E. Hicks, C. D. W. Wilkinson and J. S. Aitchison, *J. Vac. Sci. Technol., B* **16**(4), 1860 (1998).
- [9] M. Kawachi, Mitsuho Yasu and Morio Kobayashi, *Jpn. J. Appl. Phys.*, **22** (12), 1932 (1983),.
- [10] M. Kawachi M. Yasu, T. Edahiro, *Electronics Letters* **19**(15), 583 (1983).

- [11] Jesus M. Ruano, Vincent Benoit, J. Stewart Aitchison and Jonathan M. Cooper, *Analytical Chemistry*, **72**(5) 1093 (2000),.
- [12] Choon-Gi Cho, Myung Yung Jeong, Tae-Goo Choy, *Journal of Materials Sci.* **34**, 6035 (1999).
- [13] Y. T. Kim, S. M. Cho, Y. G. Seo, H. D. Yoon, Y. M. Im, D. H. Yoon, *Cryst. Res. Technol.*, **37**(12), 1257 (2002).
- [14] Sung-Hoon Jung, and Sang-Won Kang, *Jpn. J. Appl. Physics.* **40**, 3147 (2001).
- [15] J. P. Bange, L. S. Patil and D. K. Gautam, *Progress In Electromagnetics Research M*, **3**, 165 (2008).
- [16] Heiko Briesen, Andre Fuhrmann and Sotiris E. Pratsinis, *Chemical Engineering Science* **53**(24), 4105 (1998).
- [17] Takao Edahiro, Masao Kawachi, Shoichi Sudo, and Satoru Tomaru, *Jap. J. Appl. Phys.* **19**(11), 2047 (1980).
- [18] Hyungsoo Shin, Ji-Hyun Yi, Jong-Gab Baek and Mansoo Choi, *J. Material Res.* **17**(2), 315 (2002).
- [19] Choon-G Choi, Myung-Yung Jeong, Tae-Goo Choy, *Journal of Material Science*, **34**, 6035 (1999).
- [20] Tae-Hong Kim, Hee-Kyung Sung, Ji-Won Choi and Ki-Hyung Yoon, *ETRI Journal* **25**(2), 73 (2003).

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