

## **Studies on Ultra-thin Silicon–Oxynitride Grown by Laser Induced Oxynitridation in Presence of D.C. Glow Discharge**

**Manish Mishra and Rajnish Kumar**

*Department of Electronics,  
D.D.U. Gorakhpur University, Gorakhpur-273009, U.P., India  
E-mail: mmanishm@yahoo.com*

### **Abstract**

In this paper a novel technique to grow ultra – thin Silicon Oxy – nitride films using D.C. glow discharge assisted Laser induced Oxy – nitridation of silicon surface is discussed. D.C. glow discharge was created in the ambient of Oxygen and Nitrogen gases. The partial pressure of Oxygen and Nitrogen was varied keeping total pressure constant to control the nitrogen content in the film. Electrical studies on these silicon oxy – nitride films revealed an effective oxide thickness in the range of sub – nanometer with high breakdown voltage. X – Ray Photoelectron Spectroscopy (XPS) measurements on these samples confirmed the presence of nitrogen in the film.

**Index Terms:** Ultra – Thin Gate Dielectric, Silicon Oxynitride, Glow Discharge, Laser induced Oxynitridation.

### **Introduction**

From an economic point of view, conventional device and materials will continue to be employed until they become impractical. Thus, SiO<sub>2</sub> will continue to be used as the preferred choice of gate dielectric until an alternative technology becomes viable. The approach to choosing a gate dielectric with larger dielectric constant than SiO<sub>2</sub> has been to identify the materials that resemble SiO<sub>2</sub> in terms of amorphous order and band – gap. Many materials have been suggested that could replace silicon dioxide or silicon nitride as a possible gate – dielectric, e.g. the simple metal oxide as Ta<sub>2</sub>O<sub>5</sub> [1] and TiO<sub>2</sub> [2]. Other materials have been suggested, including SrTiO<sub>3</sub> [3], Y<sub>2</sub>O<sub>3</sub> [4], Gd<sub>2</sub>O<sub>3</sub> [5], ZrO<sub>2</sub> [6], HfO<sub>2</sub> [7], Pr<sub>2</sub>O<sub>3</sub> [8] and Al<sub>2</sub>O<sub>3</sub> [9].

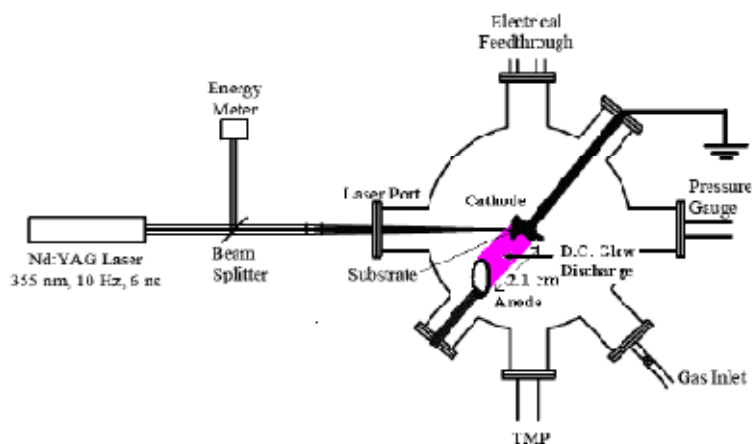
### Silicon Oxynitride as Gate Dielectric

At this time, an alternative ultra thin gate – dielectric “Silicon Oxynitride” ( $\text{SiO}_x\text{N}_y$  or, more accurately, nitrogen-doped  $\text{SiO}_2$ ) is the leading candidate to replace pure  $\text{SiO}_2$ . Oxynitride exhibit several properties superior to those of conventional thermal  $\text{O}_2$  oxides ( $\text{SiO}_2$ ), like suppression of boron penetration from the poly – Si gate and enhanced reliability. Nitrogen also reduces hot – electron induced degradation. The dielectric constant of the Oxynitride increases linearly with the percentage of nitrogen from  $\epsilon(\text{SiO}_2) = 3.8$  to  $\epsilon(\text{Si}_3\text{N}_4) = 7.8$ .

This paper focuses on another novel technique to prepare and characterize the ultra – thin gate dielectric “ $\text{SiO}_x\text{N}_y$ ” thin film using Glow Discharge in presence of oxygen and nitrogen with Pulsed Laser Heating produce ultra – thin gate – dielectric and its characterization. Traditional techniques to prepare  $\text{SiO}_x\text{N}_y$  thin films include high – temperature chemical vapor deposition (HTCVD), and reacting gas sputtering. However, the nature of these techniques limits their applications. In our process, the films are formed by heating of silicon substrate in the presence of glow discharge with a high-intensity Laser beam. The large kinetic energy of the particles impinging on the substrate surface provides a certain amount of thermal energy for surface diffusion and relaxation. As a result, high – quality thin films can be obtained without the necessity of using high substrate temperature.

### Experimental Setup

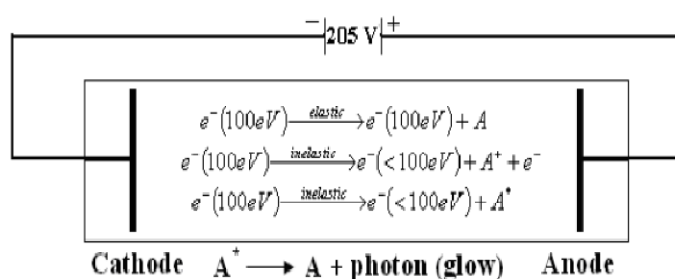
The experimental setup for controlled oxy – nitridation of silicon surface consists of a vacuum chamber, which is provided with a number of ports and windows for gas insertion, electrical feed – through, vacuum gauge and Laser etc. as shown in fig.1. Inside the chamber, the silicon substrate is placed on aluminum plate (cathode) that is grounded in the front of Copper ring (anode). The distance between cathode and anode is about 2.1 cm. The side and top windows in the deposition chamber provided a good view of deposition process.



**Figure 1:** Experimental setup.

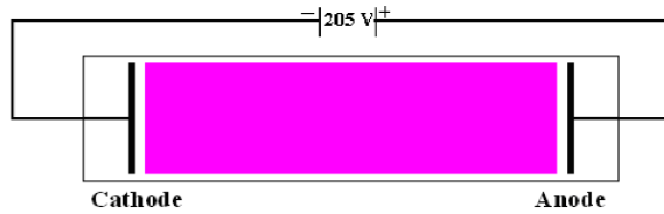
After loading the substrate, the chamber is evacuated up to  $1.5 \times 10^{-5}$  mbar with Turbo molecular pump (Turbo – V 250), which is monitored by compact full range vacuum gauge. A high – power Q – switched ND: YAG Laser with pulse duration of about 6 ns and pulse repetition frequency of about 10 Hz is used for heating the substrate. At temperatures above about  $1400^{\circ}\text{C}$ , silicon reacts with nitrogen,  $\text{N}_2$ , in oxygen, to form the Silicon oxynitride ( $\text{SiO}_x\text{N}_y$ ).

We adopted a novel technique to break  $\text{N}_2$  gas into ions at low temperature and carry out our growth in the presence of D.C. glow discharge. First,  $\text{O}_2$  and  $\text{N}_2$  gases are introduced in the chamber with partial pressure, calculated on the basis of Paschen’s Law (1889); which states that: “The breakdown voltage for a particular gas depends on the product of the pressure (p) and distance (d) between the electrodes”. Applying a potential difference between two electrodes in a gas can produce the glow. Before application of potential, gas molecules are electrically neutral. Occasionally however, a free electron may be released from a molecule by the interaction of, for example, cosmic ray or other natural radiation, a photon, or a random high – energy collision with another particle. When a voltage is applied between electrodes, say 205V/cm-torr, the free electrons are rapidly accelerated towards the anode. They quickly attain high velocity (kinetic energy) because they have such a low mass. Since kinetic energy can be related to temperature, the electrons are “hot” they achieve extremely high temperature because of their low mass, in an environment of heavy, slow moving “cold” gas molecules. Electrons begin to collide with the gas molecules, and the collision can be either elastic or inelastic (fig.2).



**Figure 2:** Breaking of gas molecules into ions.

With sufficient voltage, the gas rapidly becomes filled with positive and negative particles throughout its volume (fig.3), i.e., it becomes ionized. Then oxygen and nitrogen are easily reacting with silicon surface to form the Silicon Oxynitride. Thus, we deposit thin film of Oxynitride on silicon surface under different composition of oxygen and nitrogen (as given in table I) in the presence of D.C. glow discharge with pulse laser heating of substrate. Deposition was stopped after 40 seconds of radiation in each set of experiment.



**Figure 3:** D.C. glow discharge between two electrodes.

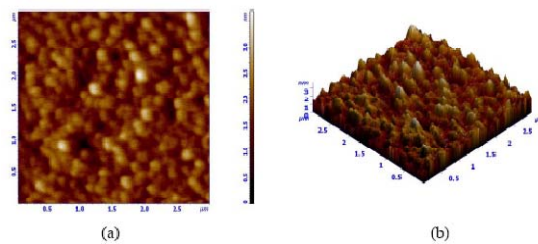
**Table I:** Different condition for growth of  $\text{SiO}_x\text{N}_y$  thin films.

Sample Number	(A)	(B)	(C)
Silicon Wafer	P-type (plane)	P-type (plane)	P-type (plane)
Base Pressure (millibar)	$1.5 \times 10^{-5}$	$1.5 \times 10^{-5}$	$1.5 \times 10^{-5}$
Partial pressure of $\text{N}_2$ (millibar)	0.999985	0.599985	1.4999985
Partial pressure of $\text{O}_2$ (millibar)	1.000000	1.4999985	0.599985
Ultimate pressure (millibar)	2.000000	2.000000	2.000000
Laser Energy (mill joule)	60	60	60
Pulse duration (ns) at 10 Hz	6	6	6
Laser beam spot diameter (cm)	1	1	1
Voltage applied (V)	660	670	650
Current (mA)	20	20	20
Distance between two electrode (cm)	2.1	2.1	2.1
Exposure time (second)	40	40	40

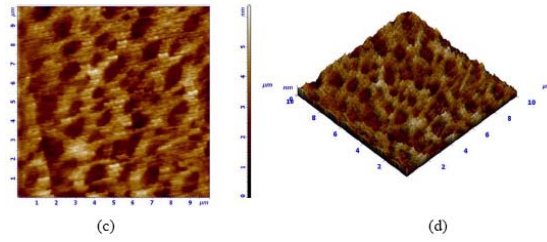
## Characterization

### *Atomic force micrographs of $\text{SiO}_x\text{N}_y$ thin films*

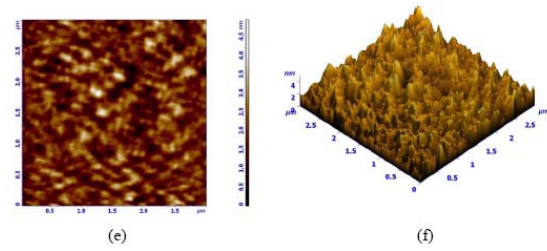
The surface morphology of the deposited  $\text{SiO}_x\text{N}_y$  thin films on silicon substrate at different composition of oxygen and nitrogen in the presence of D.C. glow discharge was examined using atomic force microscope.



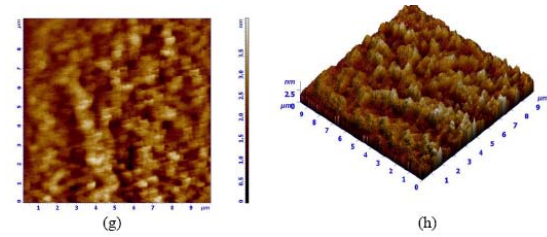
**Figure 4:** (a) 2D and (b) 3D AFM micrograph of  $\text{SiO}_x\text{N}_y$  thin film (sample A).



**Figure 5:** (a) 2D and (b) 3D AFM micrograph of  $\text{SiO}_x\text{N}_y$  thin film (sample B).



**Figure 6:** (a) 2D and (b) 3D AFM micrograph of  $\text{SiO}_x\text{N}_y$  thin film (sample C).



**Figure 7:** (a) 2D and (b) 3D AFM micrograph of bare Silicon.

**Table II:** AFM results.

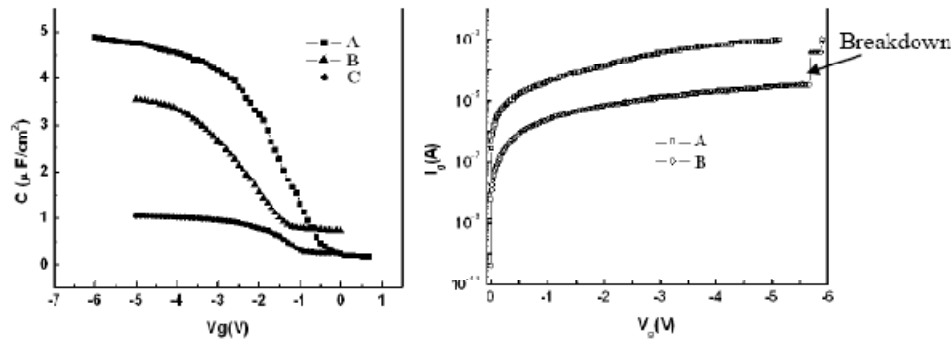
Sample Number ( $\text{N}_2/\text{O}_2$ )	RMS Roughness ( $10 \times 10 \mu\text{m}^2$ )
A (1/1)	8.1Å
B (1/3)	8.6Å
C (3/1)	7.8Å
Bare silicon	6.4Å

The photographs from (4) to (7) clearly show that the morphology is a sensitive function of composition of gases. It can be seen by comparing samples (A), (B), (C)

from the surface of bare silicon that the roughness of surface increases as the percentage of oxygen increases and nitrogen decreases. The fact is also proved by AFM result as shown in table II.

### Capacitance – Voltage and Current – Voltage characteristics

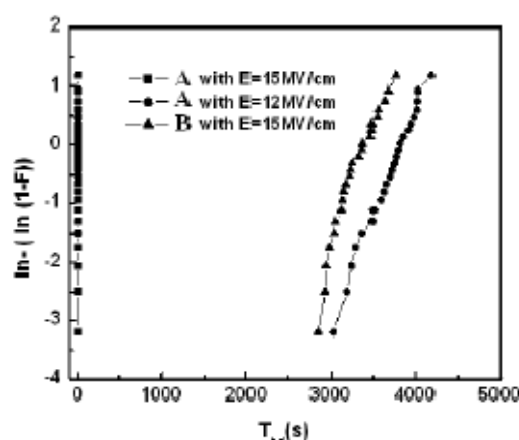
Fig.8 shows CV and IV characteristics of three samples (A), (B) and (C) of ultra – thin Silicon Oxynitride measured at 1 MHz. The effective Oxide Thickness (EOT) is calculated from accumulation capacitance [fig. 8(a)] by method proposed by Chen et. al. (2002) for ultra – thin oxide. From C-V characteristics EOT of three set of MOS capacitor (A), (B) and (C) is found to be 0.86 nm, 0.96 nm and 3.97 nm respectively. Fig. 8(b) shows typical I-V characteristics of ultra thin Silicon Oxynitride [sample (A) and (B)] that shows a good control of gate over channel. Characteristics of sample (C) are not included here because its EOT is 3.97 nm.



**Figure 8:** (a) Capacitance – Voltage and (b) Current – Voltage characteristics of ultra – thin Silicon Oxynitride

### Reliability studies using constant voltage stress

To further evaluate the insulator reliability, the ultra – thin silicon – oxynitride was subjected to constant voltage stress. Fig.9 shows the Weibull plot of  $\ln[\ln\{1-F(T_{bd})\}]$  versus  $\ln(T_{bd})$ , we obtained a straight line with slope  $\beta > 1$  (approximately). In a Weibull distribution with  $\beta > 1$  means that as the time goes on, the failure rate increases. Since from fig.9 it is clear that the time to breakdown values are in milli seconds when an electric field of 15 MV/cm is applied to the device in sample(A). The same increases to nearly 4000 s when electric field is reduced to 12 MV/cm. For sample (B), the  $T_{bd}$  values are in the range from 2800 to 3900 at an electric field of 1500 MV/cm.



**Figure 9:** Weibull plot of the time to breakdown characteristics obtained from the constant voltage stress

## Conclusion

In this work, it was possible to grow ultra – thin silicon oxynitride reliability to minimum effective oxide thickness of 0.86 nm. By conventional method was found to be difficult. From I-V characterization it is clear that silicon oxynitride shows good control of gate over channel. Therefore, the work is extremely relevant for industry to continue CMOS scaling with silicon oxynitride as gate dielectric material.

It is also possible to explore the possibility of oxynitridation of silicon in vacuum chamber under different partial pressure of oxygen and nitrogen. It could also be checked whether the oxinitridation of silicon substrate takes place without DC Glow discharge or not. The same process of DC glow discharge can be used with other substrates to find new gate dielectric for further CMOS scaling.

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