

## REACTIVE PLASMA SPUTTER DEPOSITION OF SILICON OXIDE

K.K. VOSSOUGH and C.E. HUNT

Department of Electrical and Computer Engineering, University of California, Davis, CA 95616

### ABSTRACT

Silicon dioxide films were reactively sputter deposited in argon/oxygen ambient using RF magnetron sputter deposition techniques. A substantial drop in the deposition rate at high enough partial pressure of the oxygen which is typical in reactive sputtering was observed. The best quality silicon dioxide films were obtained at the lower deposition rate, close to the deposition rate transition point. Higher quality films were obtained at higher RF powers with higher deposition rates. However, at 800 Watts RF, the so called negative ion effect dominates and results in higher surface roughness of the films, as seen by AFM results. Various characterization techniques including ellipsometry and wet chemical etching were used to compare stoichiometry and film density, respectively. MOS capacitor characterization along with breakdown voltages were also measured as a means of qualifying the films.

### I. INTRODUCTION

Reactive sputter deposition of silicon and oxide offers unique possibilities of producing nonstoichiometric thin films of silicon and oxide at low temperature. The nonstoichiometric,  $\text{SiO}_x$ , sputtered films are used in low temperature silicon wafer bonding techniques [1].  $\text{SiO}_x$  is deposited on the surfaces to be bonded. Dangling bonds or unstable chemical bonds in the nonstoichiometric  $\text{SiO}_x$  form stronger wafer bonds at lower annealing temperature. Also, the higher free energy,  $\Delta G$ , of nonstoichiometric film (compared to  $\text{SiO}_2$ ) contributes to interlayer bond formation at low temperature.

Silicon dioxide, in general, plays an essential role in modern integrated circuit technology. It is used as an insulation between conducting layers such as crossovers between metal interconnection in an integrated circuit or masking against diffusion and ion implantation of dopant impurities allowing for localized doping through etched holes in the film. Also used to protect the underlying circuit from impurities, scratches and moisture coming from the environment. Finally, it prevents electromigration in aluminium by chemically bonding with the aluminium.

Field isolation of devices on silicon using lift-off patterning of sputtered  $\text{SiO}_2$  films have been successfully utilized by Yachi et al. [2]. The Lift-Off Patterning of Sputtered  $\text{SiO}_2$  films (LOPAS) forms field oxide that is self-aligned to the channel stop region in MOSFET at low temperature. In addition to shorter process flow, LOPAS eliminates lateral Boron diffusion and bird's beak observed in conventional process.

High quality sputtered  $\text{SiO}_2$  films with good dielectric properties have also been used in multilayer (metal-insulator-metal), MIM, magnetic devices. Due to sensitivity of magnetic material and interdiffusion of the multilayer at high temperature, the low temperature reactive sputtering of  $\text{SiO}_2$  is the only option. Furthermore, a nonstoichiometric  $\text{SiO}_x$  in contact with highly oxidizing metals (i.e. NiFe) will minimize oxidation of the metal surfaces at high operating temperatures.

In reactive sputtering, a variety of sputter parameters (i.e. RF power, gas pressure, system geometry, etc.) are available to control the film quality and stoichiometry. In general, other advantages of reactive sputtering as process type include: (1) the ease of machining of metal targets, (2) high power densities can be achieved with metal targets (i.e. 50 W/cm<sup>2</sup>) because of their high thermal conductivity, and (3) fabrication of different types of dielectrics by choosing different reactive gas mixtures [3].

The dielectric coatings of oxide are deposited either by sputtering an insulating target of the insulating material ( $\text{SiO}_2$ ), or by reactively sputtering a metal target, with RF or DC power, in the ambient mixture of inert (Ar) and the reactive gas ( $\text{O}_2$ ). The reactive sputtering, however, offers high rate techniques that provide deposition rates comparable to those of pure metals. In the traditional process for reactive sputtering, the reactive gas is bled into the chamber to keep the target completely covered with the dielectric. This mode of operation, "covered mode", is limited by the low sputter yield of the dielectric. High rate reactive sputtering of the dielectric may be

achieved in the "metallic mode" which means the sputtering of the metal, with the compound formation in the gas phase or on the surface of the substrate.

Also, process modeling for reactive sputtering has been well characterized by S. Berg [4-6]. In reactive sputtering, in general, the deposition rate drops drastically at high enough partial pressure of the reactive gas. At this point the compound is formed on the target surface and sputtered rather than forming on the substrate or in the so called virtual thin film zone. Optimum properties of the compound are obtained if sputtering takes place close to this transition region at the lower rate. Since the rate of formation of the compound ( $\text{SiO}_2$ ) on the target is related to the reactive gas flow, then the deposition rate of  $\text{SiO}_2$  is related to  $\text{O}_2$  flow rate. Furthermore, at this point the target surface has changed into a multicomponent target with preferential sputtering characteristics [7]. Therefore a prolonged presputtering period is required to achieve stoichiometry and a stable deposition rate.

Reactive oxide sputtering has a unique feature; the so called negative ion effects. According to J.J. Cuomo et al. [8], target materials such as Halides and Chalcogenides (Oxygen) of the alkali metals have a large yield of negative ions that can affect the accumulation rate, composition and properties of the sputtered film. Presence of extremely electronegative elements, like Oxygen, on the target surface results in significant production of negative ions that may accelerate with full cathode potential toward the substrate. This leads to increased surface roughness of the deposited film or, at high enough  $\text{O}_2$  partial pressures, to etching of the film.

## II. EXPERIMENT

There are two objectives in using reactive sputtering technique for film deposition. These are; (a) to introduce a dopant into a metal, (b) to produce a compound (i.e.  $\text{SiO}_2$ ). According to Maniv et al. [9] there are two regions that can be conveniently separated with respect to the hysteresis curve of total system pressure,  $P$ , as a function of flow rate,  $f_r$ , of the reactive gas into the system, figure(1). The hysteresis curve of figure(1) applies, for example, to the sputtering of Si in an  $\text{Ar}/\text{O}_2$  mixture. A constant pressure,  $P_a$ , corresponding to a flow,  $f_a$ , of Ar into the continuously pumped system;  $P_a$  is the pressure at which Si target is sputtered to deposit Si films.

The hysteresis curve displays two stable regions with rapid transitions between these regions. In region A, there is little change in the total pressure as  $f_r$  is varied. In region B, the pressure varies linearly with  $f_r$  but it is lower by  $\Delta P$  than the total pressure when no sputtering takes place. In region A, almost all the reactive gas ( $\text{O}_2$ ) is consumed in the deposited film and the atomic ratio of reactive gas to sputtered metal in the film increases with  $f_r$ . Therefore, region A is considered to be the region in which the sputtered metal is doped with the reactive gas. In region B, the consumption of reactive gas is constant, independent of  $f_r$ , and there is an excess amount of reactive gas which favors the formation of a stable compound [9].

The transition from region A to B is caused by the formation of a compound on the surface of the target. In region B, some of the energy of the ions incident on the target is used to sputter the other component of the target. For example, for  $\text{SiO}_2$ , only 1/3 of the sputtered atoms are Si. Therefore, if the power is kept constant as the transition from from A to B takes place, the sputtering rate of Si atoms would decrease by at least 2/3. Less Oxygen is then consumed in the reaction needed to maintain the  $\text{SiO}_2$  layer. Thus the sputtering yield for the metal (Si) atom in the target will decrease when the compound is formed on the target surface. As the sputtering yield ratio of the metal atoms (Si) from metal and the compound ( $\text{SiO}_2$ ) increases, the value of  $\Delta P$  (figure 1) will become smaller. This means a more rapid transition from region A to B [9].

The most important factor in determining the operating point for reactive sputtering is the control of the reactive gas flow,  $f_r$ , relative to the sputtering rate. For example, to operate the target in region A, one must stay as close as possible to  $f_{r1}$ . For constant power  $P$ ,  $f_r$  is a measure of the sputtered flux. If  $f_r$  increases, the target converts to B and the deposition rate decreases. If  $f_r$  decreases, the film composition changes from stoichiometric  $\text{SiO}_2$ , to silicon rich  $\text{SiO}_x$ , with a consequent change in film properties. Since the target converts rapidly from region A to B, figure(1), the system response is not a simple linear function of  $f_r$ . Also, as the target condition changes, i.e. a more complete target erosion by  $\text{O}_2$ , the sputter rate and the flux distribution changes, thus changing  $f_{r1}$ .

During experiments, it is relatively easy to determine the value of  $f_r$  for a given value of P and system condition. Then the reactive gas flow is stopped so that target converts back to region A, and the value of  $f_r$  is increased to the operating point, just under  $f_r$ . Therefore a method of continuously adjusting the operating point to maintain a stable deposition rate and uniform film properties is necessary. The monitoring of the operating point in such a nonlinear system must be rather sensitive. For example, a significant increase in pressure will make the recovering of the operating point impossible without tracing out the hysteresis loop of figure(1). Aside from partial pressure of the reactive gas the discharge parameters, the current (I) and target bias voltage ( $V_{stb}$ ), change rapidly near  $f_{r1}$  resulting in nonhomogeneous sputtered film. All of these can be used as monitoring parameters depending upon the sputtering system and the reaction that is being controlled. To monitor an operating point near  $f_{r1}$  with target in region B, the onset of rise in reactive gas ( $O_2$ ) or the fall in voltage (which corresponds to a fall in deposition rate) is used. There would be a rapid transition from operating point, say, X to Y as  $f_{r1}$  is increased when voltage is used as the variable and where Y corresponds to  $f_{r1}$  in figure(1).

### III. RESULTS

Reactive sputtering was performed at 200 watts rf for characterization of  $SiO_2$  films. An rf power setting of 200 watts was used to minimize the substrate etching phenomenon common in reactive oxide sputter deposition. Figure 2 shows the deposition rate of  $SiO_2$  versus the percentage of oxygen in the chamber. The film thickness was measured using an ellipsometer and then verified by a differential step height profilometer. The drastic drop in the deposition rate is due to the formation of the compound on the target surface, as discussed before. The individual control of the sputtering parameters such as the oxygen flow rate and rf power are crucial in obtaining stoichiometric  $SiO_2$  with relatively high density and smooth surfaces. These optimum properties of  $SiO_2$  are normally obtained at the lower deposition rate, close to the transition region. As the oxygen flow rate is increased the condition for formation of stoichiometric  $SiO_2$  on the substrate is created. Using ellipsometry, the onset of stoichiometric  $SiO_2$  on the substrate was detected at about 4.5%  $O_2$  concentration. Up to 4.5% region, metallic Si is sputtered and then it getters oxygen. The formation of the reactive thin film ( $SiO_2$ ) takes place in the gas phase at a very short distance from the substrate in the virtual thin film. An incremental increase in  $O_2$  supply near the transition region will cause the formation of some silicon oxide on the Si target. The erosion rate of Si then decreases causing further decrease in the gettering of the oxygen. This will increase the formation of the oxide at the target even more. A runaway situation develops, resulting in a sharp transition from metallic target to a silicon-oxide target surface. Thus, the deposition rate vs.  $O_2$  flow rate plot indicates sputtering from metallic target surface at low  $O_2$  flow rate and then a shift to sputtering of the compound ( $SiO_2$ ) formed by  $O_2$  on Si target at higher  $O_2$  flow rate.

The compound sputtering is similar to any multicomponent sputtering in which the preferential sputtering of Si and  $O_2$  results in formation of nonstoichiometric film on the substrate, initially. A prolonged pre-sputtering period (about 30 min) is usually required to stabilize the deposition rate and ensure the sputtering of  $SiO_2$  species.

Chemical wet etching, BOE (Buffered Oxide Etch), was used as a measure of quality of the films. Figure 2 also shows the etch rate of the films versus the percentage of oxygen in the chamber. At low  $O_2$  concentrations, less than 4.5%, the films are nonstoichiometric and silicon rich. Therefore, the etch rate is rather low. However, at the onset of stoichiometry, greater than 4.5%  $O_2$ , the etch rate increases to about 1.2 microns per minute. From this point on, the etch rate curve follows, in parallel, the deposition curve through the transition region and beyond. The high etch rates at lower  $O_2$  concentration are clearly indicative of a lower quality  $SiO_2$  films whereas the higher quality films with etch rates closer to the thermally grown oxides (~ 1000 Å/min) are obtained at higher  $O_2$  concentrations.

The film thickness and index of refraction were measured using an ellipsometer. Figure 2 shows the index of refraction of the deposited film versus the percentage of oxygen in the chamber during sputtering. The variation in the index of refraction for a given oxygen percentage is measured across the four inch wafers. Due to the system configuration, planetary rotation of the substrate, a deposition nonuniformity is expected. Therefore, in region A or at low oxygen

concentration, the deposition nonuniformity translates into a stoichiometric nonuniformity across the wafer. Such stoichiometric nonuniformity can be attributed to the oxygen deficiencies on certain regions of the wafer surface with higher relative velocities, thus lowering the probability of Si and O<sub>2</sub> reaction just above the substrate (virtual thin film). Also, as shown in figure 2, the stoichiometric nonuniformity is not expected in region B or at high enough oxygen concentration where the sputtered species is SiO<sub>2</sub>.

Another relationship between deposition, etch rates and index of refraction versus the forward power is shown in figure 3. The deposition and etch rates were measured for a range of deposition power at 5.0% oxygen concentration. The film quality or the etch rate remains fairly stable up to about 200 watts rf where the etch rate starts to increase with increasing power and deposition rate. At this time, since there is a constant flow of oxygen into the chamber, any increase in the deposition rate will be due to the sputtering of the metallic Si which will eventually result in a sharp transition from silicon-oxide target surface to a metallic one. Therefore, figure 3 shows the onset of transition from compound to metallic sputtering. Further data on deposition and etch rates at 500 watts rf are available in Table I. At 500 watts rf the film density is significantly improved and etch rates decrease by a factor of 2. The increased density of these films is due to the higher deposition rate of the compound SiO<sub>2</sub> which results in higher pressure in sputtered flux that forms a close-pack (dense) film on the substrate.

The reactive oxide sputtering of any oxide system is plagued by negative ion effects. According to S.M. Rossnagle et al. [10] the negative ions are produced at the target surface during sputtering and are accelerated across the dark space into the plasma. The dominant species are O<sup>-</sup> ions and they attain energy by crossing the dark space to bombard the depositing film at high rate. The attached electron is stripped in the plasma and the energetic neutral atoms bombard the substrate in front of the target. The yield of the negative ions is a function of the oxygen partial pressure or its mass flow rate into the chamber. The increasing oxygen levels results in decreasing deposition rate and will eventually cause etching of the substrate at high enough O<sub>2</sub> concentration. Furthermore, even at lower O<sub>2</sub> concentrations the negative ion effect produces rough film surfaces during long deposition runs. Naturally, the surface roughness increases as the O<sub>2</sub> concentration increases.

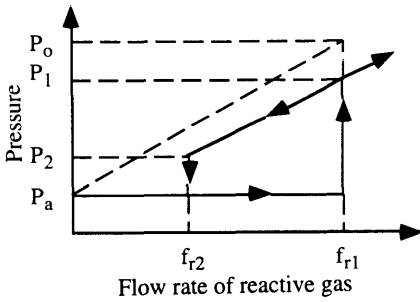
The breakdown voltages and dielectric strength across the wafer are provided in Table II. A leakage current of one micro-amp was used to determine the breakdown voltage and the variation in breakdown magnitude is due to the nonuniformity of the film thickness.

#### IV. CONCLUSION

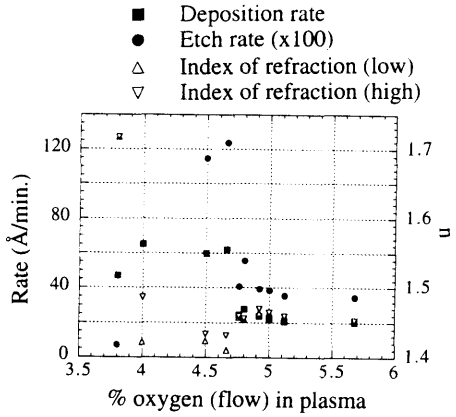
The reactive oxide rf magnetron sputter deposition of stoichiometric SiO<sub>2</sub> using rf power has been successfully examined. The deposited films are of sufficient quality to be used as insulation layers in various microfabricated devices. The reactive sputter deposition method, as opposed to sputtering of a SiO<sub>2</sub> target, is the preferred method because it can be sputtered by two completely different processes, metallic or compound sputtering, with different deposition rates and film quality. The optimum properties of the oxide films, BOE (Buffered Oxide Etch) etch rate and breakdown voltages, were obtained when the sputtering takes place close to the transition region at lower deposition rate. The film properties are nearly as good as thermally grown SiO<sub>2</sub>. Also, with careful process monitoring, it is possible to deposit nonstoichiometric silicon-oxide films.

Reactive oxide sputtering can generate large quantities of negative ions, capable of suppressing deposition rates to the point of substrate etching. The target voltage or the forward power is the major parameter affecting the substrate etch rate. The dominant ions are O<sup>-</sup> and may have effects on the properties of the sputtered film other than simple etching, i.e. increased surface roughness.

There are two interacting phenomena that limit the quality (density) of the deposited films. One is the relatively low deposition rate of the compound which produces a low pressure flux of the sputtered oxide, producing a less dense film. Second, is the negative ion effect. In conventional plasma sputtering, the film density can be improved by increasing the deposition rate (i.e. increasing forward power or working gas pressure) which results in a higher flux and higher flux pressure of the sputtered species that will densify the growing film. In the case of the sputter deposition of an amorphous film like SiO<sub>2</sub> the increased pressure results in more closely packed



**Figure 1. Theoretical hysteresis plot for system pressure ( $p$ ) versus reactive gas flow ( $f_r$ )**



**Figure 2. Index of refraction, deposition and etch rates vs. % oxygen in plasma.**

**Table I**

At 500 watts RF

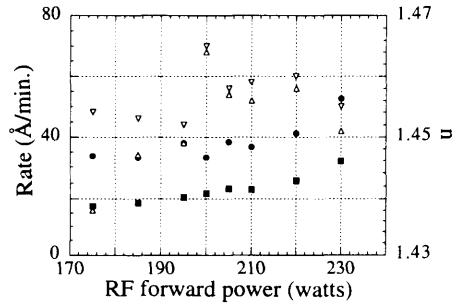
$n$ (at 633 nm)	Dep. rate (Å/min)	Etch rate (Å/min)
1.47	74.0	3027
1.46	46.3	1738
1.46	44.85	1760
1.45	54.2	1900

**Table II**

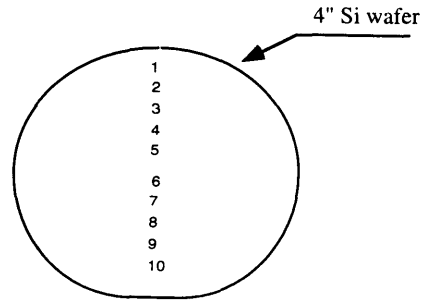
Dielectric Strength  
(for  $1\mu\text{A}$  leakage current)

- 1) 370  $\text{v}/\mu\text{m}$
- 2) 371  $\text{v}/\mu\text{m}$
- 3) 423  $\text{v}/\mu\text{m}$
- 4) 380  $\text{v}/\mu\text{m}$
- 5) 393  $\text{v}/\mu\text{m}$
- 6) 367  $\text{v}/\mu\text{m}$
- 7) 380  $\text{v}/\mu\text{m}$
- 8) 383  $\text{v}/\mu\text{m}$
- 9) 370  $\text{v}/\mu\text{m}$
- 10) 372  $\text{v}/\mu\text{m}$

Average Dielectric Strength = 381  $\text{v}/\mu\text{m}$



**Figure 3. Index of refraction, deposition and etch rates vs. rf power.**



atoms in the thin film. In reactive oxide sputtering, on the other hand, increasing deposition rate by increasing gas pressure will also increase the  $O^-$  ion concentration which yields rough film surface at low powers or etching of the film at higher power.

It may be possible to eliminate or reduce the concentration of the bombarding oxygen atoms by determining the precise mass flow rate of the oxygen being consumed by the process at any given high rf power. Then by setting the mass flow rate of the oxygen equal to the consumption rate, one can minimize the concentration of excess  $O^-$  ions while maintaining a high deposition rate.

## V. REFERENCES

1. J. A. Folta, C.E. Hunt and S. N. Farrens, *J. Electrochem. Soc.*, Vol. 141, No. 8 (1994)
2. T. Yachi, T. Serikawa and T. Wada, *IEEE Trans. Electron Devices*, Vol. ED-31, No. 12 (1984)
3. Vossen and Kern, *Thin Film Processes II*, (Academic Press, Boston, 1991), p. 191.
4. S. Berg, T. Larsson, and H-O. Blom, *J. Vac. Sci. Technol. A4*, 594 (1986)
5. S. Berg, H-O. Blom, T. Larsson, and C. Nender, *J. Vac. Sci. Technol. A5*, 202 (1987)
6. T. Larsson, H-O. Blom, C. Nender, and S. Berg, *J. Vac. Sci. Technol. A6*, 1832 (1988)
7. J.J. Cuomo, R. J. Gambino, J. M. E. Harper, J. D. Kuptsis and J. C. Webber, *J. Vac. Sci. Technol. 15*(2), March/April 1978
8. S. M. Rossnagel and J. J. Cuomo, P.106, AIP (1988)
9. S. Maniv and W. D. Westwood, *J. Vac. Sci. Technol. 17*, 743 (1980).
10. J. J. Cuomo, R. J. Gambino, J. M. E. Harper, J. D. Kuptsis and J. C. Webber, *J. Vac. Sci. Technol. 15*(2), March/April 1978