

**Invited****Advanced Low-Temperature Processing of Gate Oxide for ULSI Fabrication**

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Results are presented for low temperature (300 °C), plasma enhanced chemical vapor deposition of gate insulators, in which MIS performance is related to variations in interfacial chemistry and network connectivity.

**(1) Introduction**

A strong, general trend toward lower process temperatures and the development of device structures such as TFTs or SiGe-base HBTs, requiring insulator deposition, as opposed to direct oxidation, have fueled research activity in low temperature, plasma enhanced chemical vapor deposition (LT-PECVD) processes for gate insulator formation. A key issue in this research is the stability of LT-PECVD films under stress testing. This paper presents results from two types of studies directly relevant to stress performance: (1) studies of the relationship between the bulk properties of LT-PECVD SiO<sub>2</sub> and process parameters, particularly plasma power; and (2) studies of the interface formation chemistry, both for single layer oxides and for more complex multilayer oxide/nitride/oxide (ONO) structures.

**(2) Research Results**

*Interfacial Effects:* MIS formation using deposition processes are sensitive to surface contaminants. For best results these must be removed using in situ or in line processing. Carbon removal from the starting surface is essential to obtain low  $D_{it}$  and stable interface performance. Brief (30 sec), plasma activated hydrogen exposure effectively removes C, but surfaces treated with hydrogen, although exhibiting low  $D_{it}$  ( $2 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ ) have high rates of interfacial generation

of minority carriers. A further disadvantage of hydrogen based cleans, particularly for the (100) surface, is that the Si surface is etched through attack of the Si backbonds; this leads to surface roughening and, if carried to an extreme, microfaceting. An attractive option for MIS formation is direct exposure of the surface to plasma active oxygen at 200 °C. This typically results in 0.6 nm of oxide formation and is effective in removing carbon. There is no evidence of any roughening as a result of this process. Moreover with direct oxygen exposure prior to oxide deposition, deep depletion is observed in both the quasistatic and the high frequency characteristics indicating low rates of interfacial generation of minority carriers. This effect is shown by direct comparison in Figures 1 and 2. Direct oxidation prior to deposition also effects the response under constant current injection stress testing. Conventional thermal oxides typically show a flatband change of 50 mV after injection of  $2 \times 10^{-4} \text{ C-cm}^{-2}$  accompanied by an increase in interface state density of  $1.9 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ . When deposition is preceded by direct oxidation, LT-PECVD films show a flatband change of 200 mV accompanied by an increase in interface state density of  $1.5 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ . This performance is comparable to thermal oxides but not yet equivalent. In considering the effect of direct oxidation it should be realized that LT-PECVD by itself also results in direct oxidation of the interface. Studies [1] of this phenomena show that there are two components of direct oxidation during the deposition process. First a rapid oxidation

of the original surface at the onset of the deposition process, followed by a much slower subcutaneous component during the remainder of the deposition. At 300 °C the net interfacial oxidation during the deposition of a 15 nm oxide is 0.9 nm. The subcutaneous process is essentially self-limiting in this temperature range. This thickness is directly comparable to the thickness observed following direct oxidation at the same temperature. However the electrical performance of the resultant MIS structure (using no direct oxidation) is very different from the case where direct oxidation is used. This is in spite of the fact that the oxidized thickness is virtually the same for the two cases. Stable interfaces relate strongly to the distribution of Si oxidation states found at the interface. Direct oxidation of the surface by plasma activated oxygen results in less spectral weight associated with the components of the +2 and +3 oxidation states in a Si 2p XPS spectrum than is observed for the interfacial oxides formed during the LT-PECVD process. These differences in oxidation state distribution in the near-interfacial region are an important element in determining the response of LT-PECVD MIS structures under current injection-based stress testing. In addition to direct oxidation of the surface prior to oxide deposition an ONO structures with interfacial oxides in the thickness range of 1 to 2 nm can be used to limit the extent of the subcutaneous oxidation component.

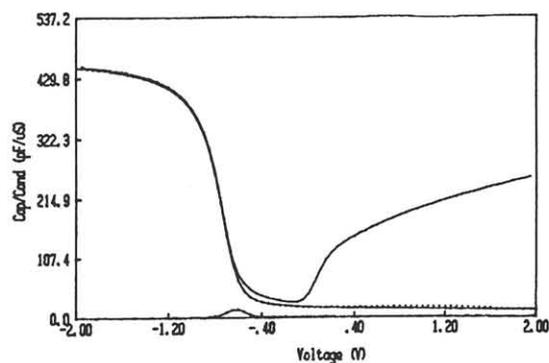
**Bulk Properties:** LT-CVD oxides can differ from conventional thermal oxides in two important ways: stoichiometry and networking. Of course bonding defects and stoichiometry variations, such as Si-rich compositions (suboxides), are accompanied by trapping phenomena, particularly evident during current injection. A signature of suboxide character is a downward shift in stretch frequency (relative to thermal oxide) and an increase in FWHM. Less well understood are the effects of networking differences. When low temperature thermal oxides are annealed and their response to annealing is plotted as refractive index versus Si-O-Si stretch frequency, a linear relationship is observed [2]. Similarly when LT-PECVD oxides are annealed, index versus stretch frequency plots are also linear with annealing [2]. However the index versus stretch frequency change for the LT-PECVD films as a function of annealing are fundamentally different from that of thermal oxides. When identically plotted, data from the two types of samples evidence different slopes. With no IR evidence of suboxide behavior, this slope change

may be attributable to networking differences [2]. Networking is also strongly evidenced in the etch rate of LT-PECVD oxides. As plasma power is increased from 10 W to 300 W (all other conditions constant) the etch rate falls by 15X using P-etch, (15)HF:(10)HNO<sub>3</sub>:(300) H<sub>2</sub> O. A 300 W LT-PECVD sample has an etch rate within experimental error of thermal oxide. As might be expected based on the etch rate data, when plotting refractive index versus stretch frequency, the 300 W sample falls on the thermal oxide annealing line, corresponding to a 700 °C thermal oxide. The data relating refractive index and stretching frequency is shown in Figure 3. Thus high power RF discharges result in low temperature production of deposited oxides with bulk networks characteristic of thermal oxides grown at far higher temperatures, as evidenced by etch rate and the relationship of refractive index and Si-O-Si stretch frequency. Pronounced effects of power density have also been observed in SiO<sub>2</sub> deposited in parallel plate reactor configurations [3].

### (3) References

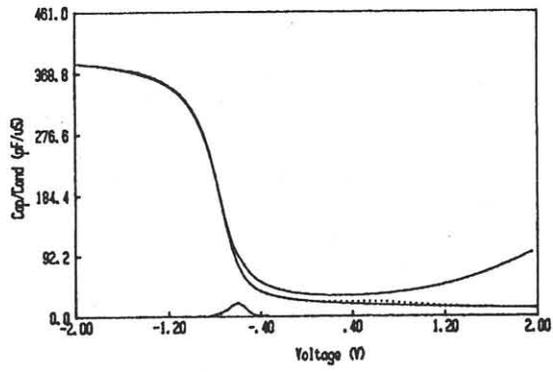
- 1) S.V. Hattangady, M.J. Mantini, G.G. Fountain, R.A. Rudder, and R.J. Markunas, J. Appl. Phys. 71(1992) 3842.
- 2) G. Lucovsky, J.T. Fitch, D.V. Tsu, and S.S. Kim, J. Vac. Sci. Technol. A 7(3)(1989) 1136.
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### (4) Figures



**Hydrogen plasma + oxygen plasma  
in situ surface treatments.**

FIGURE 1



Oxygen plasma in situ surface treatment only.

FIGURE 2

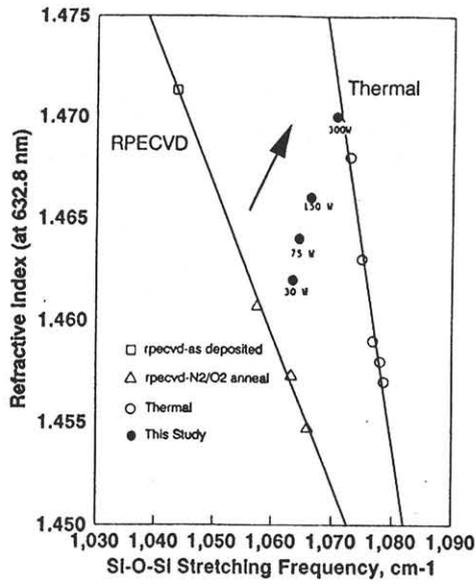


FIGURE 3