It has been recently reported from our laboratories\(^1\) that MOS structures containing oxides grown in an \(O_2\)-HCl ambient possess considerably better electrical stability under positive bias-temperature stress than identically contaminated MOS structures prepared from silicon oxidized in pure \(O_2\). The main cause of instability in MOS-type devices is the migration of positively charged ions in the oxide to within a short distance of the silicon interface, where the ions remain effectively charged and therefore exert a large influence on the silicon surface potential. Experimental evidence has indicated\(^2,3\) that the "passivating effect" observed in MOS structures prepared from "HCl oxides" is due to the trapping and neutralization of positively charged ions as a result of their interaction with chlorine near the silicon interface. The passivation appears to be equally effective against contamination introduced unintentionally during device processing and against intentional sodium contamination of the MOS structure produced by the evaporation of a sodium compound onto the oxide surface prior to metallization with "clean" aluminum. This paper will discuss the physical basis of some important aspects of the use of HCl passivation in MOS processing technology and will report on the characteristics of HCl processed p-channel MOS field effect transistors.

It has been observed that, for a particular method of sample preparation, the fraction of the total mobile charge that is passivated during positive bias-temperature stress is essentially independent of the level of sodium contamination up to at least \(5 \times 10^{12}\) ions/cm\(^2\). Since the drift of sodium ions in the oxide can be assumed to take place in the direction of the applied field, and the surface concentration of ions is well below a monolayer, this result allows the assignment of a "trapping cross section" to a given sample. However, this cross section is not a linear function of the HCl concentration used during the oxidation, but rises very quickly over a narrow range of HCl concentrations. This sudden rise may either coincide with a very rapid increase of the volume concentration of chlorine in the oxide near the silicon interface, or it must indicate that the efficiency of the trapping and neutralization mechanism is a steeply increasing function of the distance between the impurity chlorine sites in \(SiO_2\). The sudden onset of strong passivation is also observed at a fixed HCl concentration as the duration of oxidation increases.
Once a high degree of passivation (~95 - 99%) has been achieved, any further increase in the HCl concentration or prolongation of the HCl treatment results in an increasingly "grainy" appearance of the oxide. Oxides grown on (111) silicon surfaces are more liable to show this effect than those grown on (100) orientation. Examination of the grainy samples by electron microscopy shows that while a considerable "bumpiness" is observed on the oxide itself, the silicon surface underneath remains much smoother. This explains why, although some difficulties may be experienced in the photoengraving of such oxides, the characteristics of MOS field effect transistors made with slightly grainy gate oxides are similar to those prepared with standard oxides. Apart from the improved stability, other parameters such as turn-on voltage, current-voltage characteristics, gate breakdown and source/drain to substrate breakdown, were found to be essentially unaffected by the HCl treatment. While most of the experiments to date have been performed on Al-gate transistors, some preliminary measurements on silicon-gate devices indicate that the passivating characteristics of the gate oxides are not adversely affected by further high temperature processing; these results are promising for the development of a silicon gate technology entirely without the use of either a double layer dielectric or phosphosilicate glass passivation.

(3) R.J. Kriegler, J.D. Morris and D.R. Colton, Paper 280, Presented at the 1972 Fall Meeting of the Electrochemical Society, Miami Beach, Florida.