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Selective Plasma Oxidation of GaAs

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Extensive research on the plasma oxidation of GaAs has been carried out in recent years.⁽¹⁾ It has been shown that plasma grown oxides are not only homogeneous and amorphous in nature, but also dense and dry. Auger depth profiling combined with Rutherford backscattering and ion induced x-ray measurements show that plasma grown oxides are both uniform in depth and have a Ga/As ratio near unity in the bulk of the oxides.⁽²⁾ Preliminary results on MOSFET devices made with plasma grown oxides are quite promising.⁽³⁾ However, more detailed studies on the composition of these oxides by a variety of analytical techniques (such as AES, TEM, Spectroscopic Ellipsometry, Raman Scattering, etc.) show the existence of elemental As in the oxide and especially at the oxide-GaAs interface even though the width of the interface is only about 50Å.

The excess elemental arsenic is deleterious to the electrical properties of MOS structures because they give rise to high interface state densities and create a large hysteresis in the C-V curve. The arsenic layer at the interface is stable even under high temperature anneal; in fact, upon anneal in nitrogen gas, the arsenic layer crystallizes into thin metallic domains at the interface, thus severely disrupting the electrical communication between the oxide and semiconductor.⁽⁴⁾ Hydrogen apparently reacts with the oxide and the arsenic layer at 450°C and can essentially eliminate the hysteresis in the C-V curve, but it also causes the oxide to become leaky, because the compounds in the oxide containing hydrogen are not good dielectrics. Growth parameters can be altered, and surface filter films can be advantageously utilized to reduce the arsenic accumulation at the interface, but these methods have not been successful in completely eliminating the hysteresis in the C-V curves AND preventing the oxide from being leaky at the same time.^(5,6) These difficulties led us to the possibility of applying selective reactions for eliminating the elemental arsenic at the interface in particular.

The key to the success of such an endeavor is the identification of the proper reactant. The desirable properties of the reactant are as follows:

- (1) It should be a gas which can form a plasma that can co-exist with the oxygen plasma and without reacting with it.
 - (2) The reactant should react more readily with arsenic than with gallium, and should preferably form a volatile compound.
 - (3) This added reaction should not compete with the formation of arsenic oxide.
- An element that satisfies these conditions is fluorine. It forms AsF_3 with a (gaseous) heat of formation of 218 Kcal/mole, whereas the heat of formation for gallium fluoride is only about 38 Kcal/mole. In addition, arsenic fluoride is fairly volatile, which means that it can be removed upon annealing.

Therefore, oxides were grown using mixtures of O_2 and CF_4 gases at CF_4/O_2 ratios between 0.1 and 3 with background pressures below 10^{-3} Torr. The plasma thus formed contains a mixture of CF , CO , and CFO complexes as well as O_x^- , F^- , and electrons. By biasing the GaAs substrate positively with respect to the plasma, we can expect to collect F^- , O_x^- , and electrons for oxidation. Oxides formed by this selective process have the following properties: (1) The oxide is essentially stoichiometric (except for the presence of fluorine), i.e., the Ga/As concentration ratio is nearly unity throughout the oxide. (2) There is essentially no hysteresis in the C-V curve, indicating trap states have been removed. (3) The C-V curve goes into inversion, indicating that the oxide does not leak.

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