USE OF A MULTIPOLE PLASMA FOR THE OXIDATION OF GaAs

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ABSTRACT

A multipole plasma source is described and its use for oxidizing GaAs is demonstrated in the case of O_2 and $CF_4 + O_2$ plasmas. The advantages of this system with respect to more conventional plasma sources (DC or RF discharges) are discussed.

1. INTRODUCTION

Plasma oxidation is a rather new technique in the study of GaAs M.O.S. structures and encouraging results have recently been obtained by this method [1][2]. This technology can be integrated in a whole device fabrication scheme in a high purity controllable method (U.H.V.).
We describe here the oxidation of GaAs in a multipole [3] plasma, which has several advantages with respect to more conventional plasma sources (RF or D.C. discharge).

2. EXPERIMENTAL

Our multipole system is shown on figure 1. An arrangment of 20 columns of permanent magnets mounted on the walls of a non magnetic stainless steel cylinder (diameter 15 cm, height 30cm) and presenting alternatively their north and south pole towards the plasma confines the primary electrons emitted by a hot filament, which is biased negatively (20-50V) with respect to the walls.
This magnetic confinement is completed by two discs with permanent magnets at both ends of the chamber.
The sample is placed on a small copper disc which is temperature regulated. The edges of the sample are covered by an alumina cap. With this geometry the sample surface is the only anode in the

plasma.

The system has the following advantages :

a) - the magnetic confinement leads to higher plasma densities at given electron emission and gas pressure. In our device, oxygen plasma densities up to 3×10^{11} cm^{-3} have been measured with a thin Langmuir probe with pressures ranging from 5×10^{-4} Torr to 3×10^{-3} Torr.

b) - Because the primary electron travel length is much larger than the multipole dimensions, the plasma is statistically homogeneous in a large volume and oxide layers are uniform in thickness over large areas.

c) - the multipole operation requires only modest D.C. voltages (generally under 50V). R.F. radiation damages and cathode sputtering which can be serious drawbacks in other kinds of plasma discharges are thus avoided. No cathode contamination, sometimes reported by other authors [4], was observed in our oxides either by SIMS or by Auger spectroscopy.

Oxidations have been carried out on samples with [100] orientation V.P.E. grown n (4×10^{16} cm^{-3} to $2 \times 10^{18} cm^{-3}$) and p ($7 \times 10^{15} cm^{-3}$) layers on heavily doped n^+ and p^+ substrates. The oxidation process was monitored by in situ ellipsometry (He - Ne laser). The current density through the sample was kept constant.

a) - Rate of oxidation

Fig. 2 gives the growth kinetics of a typical oxide. The plasma density was about 3×10^{10} cm^{-3} the current density $50 mA/cm^2$ and the substrate temperature 40 to 50 °C. The oxidation rate is approximately constant ($\sim$300 Å/min) as long as the thickness is below 1200 Å(The initial slow oxidation rate corresponds to the period when the plasma is generated but no bias voltage is applied to the sample) The origin of this phenomenon, which has also been observed in DC plasmas is not clear. If the oxidation was performed at constant bias voltage, the equivalent effect was the fact that the current density decreases with time but does not go to zero but reaches a residual value (about 20% of the initial density). This has also been observed in DC plasmas [4].

One possible explanation would be the back sputtering of the oxide by oxygen ions from the plasma. In this case, the saturation would correspond to the instant where the sputtering rate has increased enough to equal the oxidation rate.

Indeed, the existence of a significant ionic sputtering is doubtful, due to following fact. If, after having grown a certain thickness of oxide, the sample bias voltage is reduced below a certain threshold, the thickness holds a constant value (the electric field in the oxide is below the breakdown field necessary for the ionic diffusions) but does not decrease.

b) - Comments upon the oxidation mechanism

At least in the multipole and RF discharge plasmas, the oxidation mechanism seems to be an in-diffusion of oxygen ion associated with an out-diffusion of gallium and arsenic. This is suggested by oxidation experiments carried out on Al GaAs or Si/GaAs at Bell Labs and at LEP. After oxidation GaAs oxide is found on both sides of the aluminium or silicon layer which is itself oxidized.

In order to find the origin of the oxygen ions involved in the mechanism oxidations were made with two permanent magnets mounted near the sample with the magnetic field (a few hundreds gauss) parallel to the GaAs surface. The current incoming on the sample is then drastically reduced. The electron contribution of the current is suppressed because the magnetic field keeps the electrons away from the sample surface while the ions are not affected. Under these conditions the oxidation rate is strongly reduced. This experiment provides clear evidence that the electron contribution to the current plays an essential role in the oxidation process, by creating through a still poorly known mechanism, (e.g. dissociative attachement) the oxygen ions involved in the oxidation. It also clearly indicates the relative magnitudes of the electronic and ionic parts of the sample current.

3. PROPERTIES OF THE OXIDES

3.1. - Composition

The composition of the oxides and the interfaces was studied by SIMS and Auger spectroscopy. Auger profiles were made quantitative by using standards.

The main features are :

. an almost flat profile in the major part of the oxide with typical atomic concentrations of O : 50%, Ga : 35%, As : 15%. The bulk of the oxide is therefore arsenic deficient ;

. a superficial layer (of about 200 Å for a 1000 Å thick oxide) presenting an increase of the As concentration and a decrease of the Ga concentration ;

. an oxide-semiconductor interface presenting an arsenic excess. The interface width is estimated at about 100 Å, by taking it to be the depth over which the oxygen concentration falls from 90% to 10% of its maximum value.

After annealing in nitrogen at 350 °C for 30 mn the bulk concentrations are almost unchanged (except for the superficial layer where the As concentration increase disappears), but the interface seems to be somewhat sharper.

The overall deficiency in arsenic is very likely explained by the higher volatility of the arsenic oxides compared with the gallium oxides.

The deficiency in arsenic and the arsenic excess have been observed in other plasma grown oxides [4] [5]. However the interface width depends on the oxidation conditions and especially on the oxidation time : a sharp interface corresponds to a short oxidation time.

3.2. - Physical properties

The oxides were amorphous as demonstrated by X-ray diffraction. The optical properties were measured by reflectometry and spectroscopic ellipsometry with good agreement between the two methods.

Fig. 3 gives the spectroscopic ellipsometry analysis on two typical samples : one 1700 Å oxide layer grown in O_2 plasma and another one, with the same thickness and oxidation rate (as monitored by in situ ellipsometry) grown in a 70 % O_2 + 30% CF_4 plasma. Fig. 3a gives the complex reflectance ratio $R_p R_S^{-1} = \tan\psi \exp(i\Delta)$ as a function of energy for the two samples. Fig. 3b gives the corresponding dielectric functions of the layers, calculated from Fig. 3a, assuming an infinitely sharp interface between the oxide and the GaAs substrate. In both cases, the most interesting feature is the long absorption tail of ε_2 which remains finite even at low energies (below 3.5eV). This has already been observed on other plasma grown oxides [6] and is a marked difference with anodic oxides [7]. Some absorbing material is therefore present in the oxide, most likely unoxidized As. Following a suggestion by R.P.H. CHANG, the use of CF_4 in the O_2 plasma was meant to reduce this amount of unoxidized As by forming As F_3 compound. As seen in Fig. 3b, the fluorine-containing oxide is slightly less absorbant and the absorption edge is shifted towards higher energies. Furthermore, oscillations in ε_2 are far less pronounced in the case of CF_4 + O_2 plasma. Those oscillations are due to the existence of an interface between the oxide and the substrate and illustrate the non validity of the above assumption (three-phase model) [6]. Clearly, the importance of the interface region is less pronounced with the fluorine-containing layer, i.e. the interface is sharper.

3.3. - Electrical properties

The electrical properties of the oxides were investigated by M.O.S. C(V) measurements.

The results are similar to those of other authors [4]. Interface states densities in the 10^{13} cm^{-2} eV^{-1} range are located near midgap and prevent M.O.S. structures on n type samples to be biased up to accumulation. On the other hand C(V) measurements at very high frequency (above 1 MHz) or at low temperature on M.O.S. structures on p type samples have evidenced faster interface states located in the lower half of the band gap.

Some improvement was obtained, especially in reducing the hysteresis, by anodizing Al/GaAs or Si/GaAs structures.

Comparative measurements on oxides grown in a CF_4/O_2 mixture are in progress.

However, the interface states should not severely restrict the microwave properties of MOSFET transistors working in depletion or enhancement mode, because they are unable to follow input signals in the GHz frequency range [2].

CONCLUSIONS

The multipole is a very convenient plasma source which can easily produce a high density homogeneous plasma.

Uniform (over $2cm^2$) GaAs oxides have been obtained with typical growth rates of 200 Å/nm.

The electrical properties are still insufficient for inversion type MOSFET but allow the fabrication of depletion and enhancement type MOSFET.

Elaborate investigation techniques (spectroscopic ellipsometry) are presently used in this work to obtain a better knowledge of the interface oxide-GaAs in order to improve the electrical properties.

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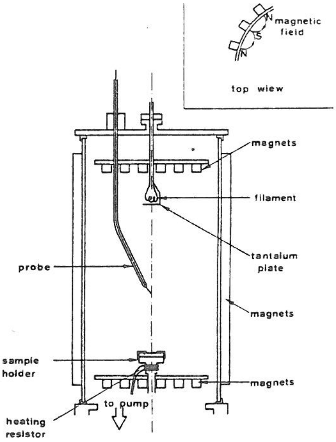
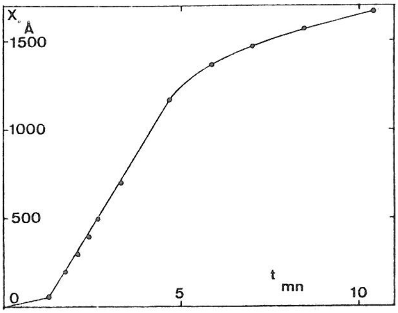
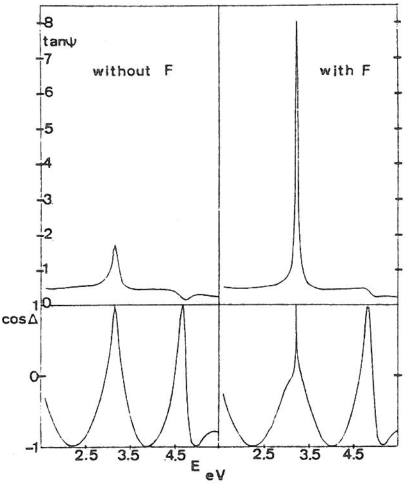


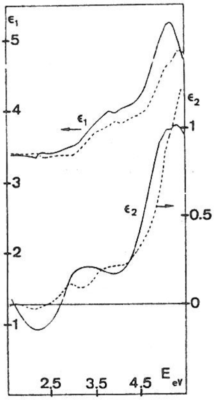
The multipole chamber (insert shows a partial top view with the azimuthal magnetic field).



Oxide thickness as a function of time.



a- Complex reflectance ration $R_p R_s^{-1}$ = tan ψ exp (iΔ) as a function of energy (with F = 70 % O_2 + 30 % CF_4 plasma ; without F = O_2 plasma)



b- dielectric functions $\varepsilon = \varepsilon_1 + i\,\varepsilon_2$ calculated from a) in a three-phase model(dashed lines = O_2 + CF_4 plasma;solid lines = O_2 plasma)