

# ELECTROLYTIC OXIDATION OF SEMICONDUCTOR SURFACES

H. L. HARTNAGEL

*Department of Electrical and Electronic Engineering, University of Newcastle upon Tyne, NE1 7RU. U.K.*

*(Received December 23, 1976)*

Recently a greater understanding of the physics and chemistry of anodic oxide growth on III-V compound semiconductors has become available. These details are reviewed and critically assessed. With the data available now new device applications can be considered.

## 1. INTRODUCTION

The technology of Si is very advanced. After initial efforts to fabricate SiO<sub>2</sub> by electrolytic methods, this was abandoned because of the small Faradayic efficiency, particularly when thermal oxidation of Si turned out to be very successful.

Unfortunately, high-temperature processes are difficult for many of the compound semiconductors where a highly volatile component is involved. Indeed, attempts to achieve thermally grown native oxides on such materials as GaAs, GaP and InP, have not been successful because decomposition of the semiconductor occurs by evaporation of As or P before any oxide is grown so that the semiconductor surfaces and interfaces become severely degraded.

It is possible for some of these materials to produce oxide layers by a reasonably-low-temperature process. However, even then the electrical interface properties are not satisfactory. Probably, the semiconductor surface layer underneath the oxide becomes severely degraded due to the large difference in self-diffusion coefficients of the components involved (see<sup>1</sup>, pp. 416–421). Some improved results have been reported by plasma discharging under suitable conditions<sup>2</sup> when, however, the interface characteristics and the oxide conductivity are still unsatisfactory for most applications.

The electrolytic oxidation methods were therefore used on these semiconductors and, under certain conditions, surprisingly high Faradayic efficiencies were achieved.<sup>3</sup> Further developments since then have resulted in an oxidation technology with oxide characteristics suitable now for many applications.

There are of course numerous applications where a

high quality oxide layer is of interest. Firstly one has the possibility of replacing the MESFET by a MOSFET<sup>4,5</sup> in these compound semiconductors for those areas where the Schottky gate has shown serious disadvantages. MESFETs are easily damaged by high currents applied to the gate, and this is particularly serious for amplification of higher power levels. They are also difficult to operate in integrated digital circuits because of the bias level requirement to the gate demanding always reverse bias to avoid any damage and because of the relatively high standby power. This latter point will be specially well provided for by normally off inversion-layer MOSFETs.

Secondly, with the new understanding of compound-oxide electrolytic growth,<sup>6</sup> it is possible to produce layered structures of high uniformity with charge injection properties and extremely stable non-volatile memory characteristics. This will be of interest for memories of gigabitrate read-out facilities by producing MAOS FETs in GaAs<sup>1,3</sup> (Metal – aluminium oxide – native oxide – semiconductor FETs).

Further possibilities exist in the optical field where the highly transparent native oxide placed on hetero-junction laser mirrors can be used to act as an anti-reflection coating. Further optical applications will surely be established by additional experimentation, such as a reduction in any surface recombination velocity which is some times the cause for thermal breakdown of semiconductor lasers.

Native oxides can also be valuable for planar monolithic circuit production, in a similar manner as SiO<sub>2</sub> on Si. Or it can be used to passivate any device surfaces against corrosion and other long-term effects.

## 2. THE PHYSICAL PROCESS OF ANODIC OXIDATION

A considerable amount of experimental data makes it very likely that the following process is involved for anodic oxidation. When the semiconductor is inserted into an aqueous solution with its high dielectric constant, the surface atoms of the semiconducting material are dissolved into the liquid as their ionic bonds are weakened. The atoms enter the liquid as multiply positively ionised species, such as  $\text{Ga}^{+++}$  or  $\text{As}^{+++}$ , leaving on the semiconductor surface an immobile negative charge which has to be neutralised by mobile holes from the bulk of the semiconductor. After a second electrode is placed as cathode electrode into the solution, the semiconductor can be employed as anode with a positive potential which aids the hole flow to the semiconductor surface so that more ions can be released. These ions travel towards the cathode.

If sufficient ions are released they form a dense ionic cloud in front of the anode. This is particularly easy if either the solubility or the diffusion coefficient of these ions is reduced by the introduction of a suitable liquid into the aqueous solution. It was found that some liquids are particularly effective, such as glycol.<sup>3</sup>

The ions in this cloud will capture  $\text{OH}^-$  ions of the aqueous solution, and, with the simultaneous formation of  $\text{H}_2\text{O}$ , are oxidised. It is likely that most of them will form well-known oxides such as  $\text{Ga}_2\text{O}_3$  or  $\text{As}_2\text{O}_3$ , which will exceed a density saturation level in this cloud so that they begin to precipitate against the semiconductor. An oxide layer begins to get deposited thus.

Further growth is now only possible if ionic transport takes place across the oxide. Each of the ionic species has a threshold field for drift and a specific value of mobility.<sup>1,2</sup> With normal current densities applied across the semiconductor surface which is immersed into the electrolyte, the fields across the oxide and its interfaces are sufficiently high for the motion of all ions, namely  $\text{OH}^-$  and the positively ionised components of the semiconductor. However as the mobility of  $\text{OH}^-$  is much smaller than that of the multiply ionised components, the primary growth occurs at or near the electrolyte-oxide interface. Unfortunately, the current density cannot be reduced beyond a minimum value which is different for each material. This value has sometimes been called the dissolution current as it seems to agree with the equivalent cation current due to the dissolution of the oxide in the electrolyte when no external

current is applied. It can be understood as the flow of those cations which, after dissolution from the oxide, successfully leave the anode region. Only when this minimum current density is exceeded, can growth take place. This means that with the electrolytes known so far, native oxides on most III-V Compound Semiconductors such as GaAs, can only be produced after exceeding the drift threshold for all the ionic species involved.

However, Al and some other metals have a very small dissolution current. After depositing a layer of such a metal by evaporation on top of the semiconductor, this metal will first be oxidised in the electrolyte. After it has been completely transformed, the oxidation of the semiconductor begins. For a high current density, the semiconductor components drift as cations across the  $\text{Al}_2\text{O}_3$  and native oxide of the semiconductor appears on top of the  $\text{Al}_2\text{O}_3$ . On the other hand, for a low current density the semiconductor components cannot become mobile, and it is only  $\text{OH}^-$  which crosses the  $\text{Al}_2\text{O}_3$ . Correspondingly, native oxide of the semiconductor appears only between  $\text{Al}_2\text{O}_3$  and the semiconductor. It is therefore possible to produce various types of layered structures. It is useful to consider this now systematically for various types of device applications.

## 3. QUANTITATIVE ANALYSIS OF OXIDE GROWTH

The oxide growth can be undertaken either with a constant-current source or with a constant voltage supply in series with a sufficiently high series resistance in order to limit the initial current density. A voltage supply without such a limiting resistance is not advisable as the initial current density can easily become so high that hot spots and other detrimental effects can occur during the initial stage of growth so that a deterioration of the oxide quality appears. A constant-current case would require a voltage measurement between cathode and anode in order to monitor the growth procedure. A voltage and series-resistance arrangement can enable one to monitor the growth by measuring the current flowing across the electrolytic cell. For the relatively high final growth voltages involved across most of the oxides of device interest, it is not required to undertake the more refined electrochemical potential measurements as these would then be normally a negligible fraction of the applied voltage.

It is possible to model the growth behaviour relatively satisfactorily by a simple treatment,

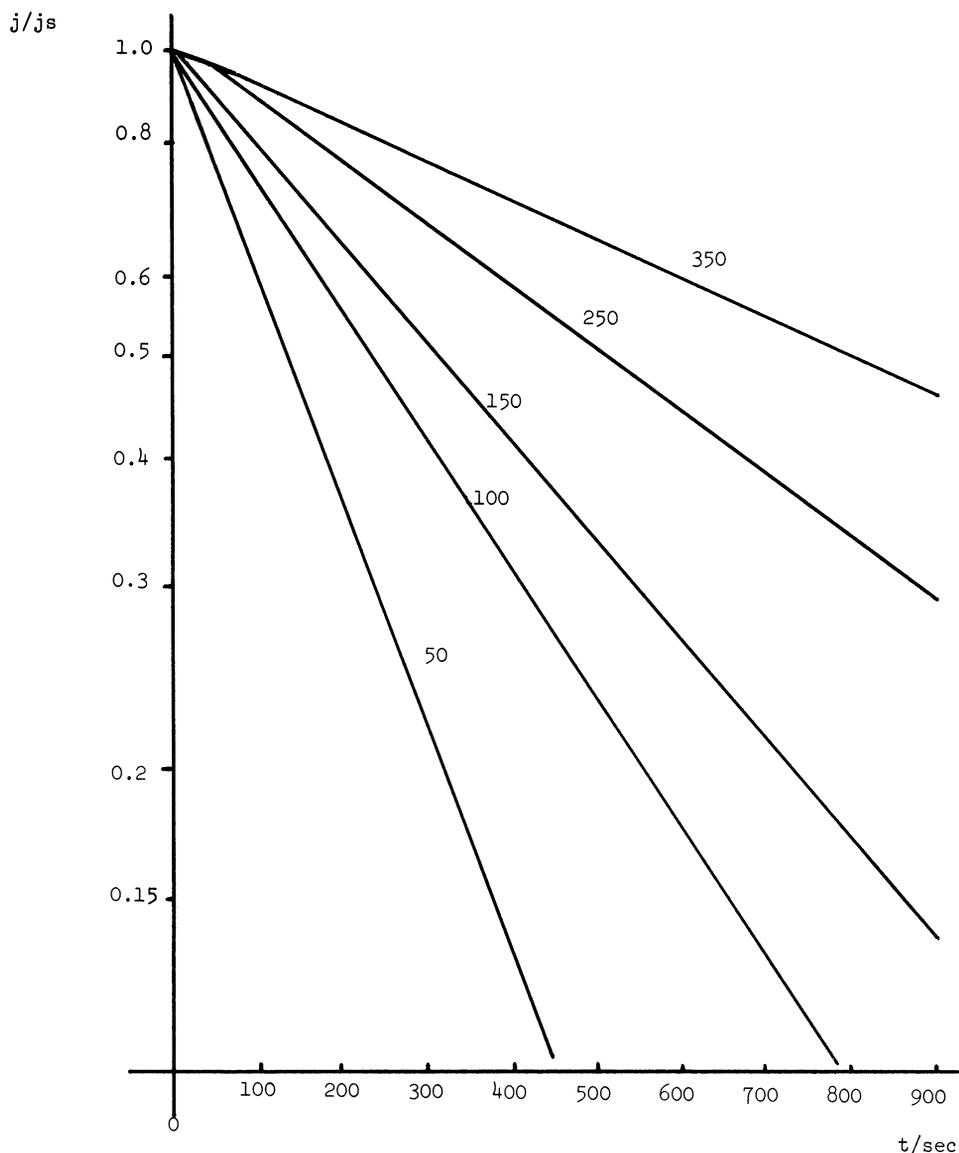


FIGURE 1 Normalised anodisation current density  $j$  vs. time  $t$ .  $j_s$  – initial current density,  $j_s = 1 \text{ mA/cm}^2$ ; the parameter is the externally applied voltage in volts.

provided that precautions are taken for a uniform current density across the semiconductor surface which is exposed to the electrolyte. By way of example, this is to be outlined here for the constant-voltage plus series-resistance arrangement. The treatment of the other case of growth is very similar.

The general current functions measured are shown in Figure 1. A typical experimental set up is given in Figure 2, where it is also indicated that a light source

is needed in order to have sufficient holes available for the neutralization of the negative surface charge created by the removal of positive cations. This illumination is particularly important for  $n$ -type material where practically no holes would be present otherwise. Failing to provide a sufficient supply of holes means that the space charge layer set up by the negative surface charge caused by the departing cations absorbs a substantial part, if not all, of the

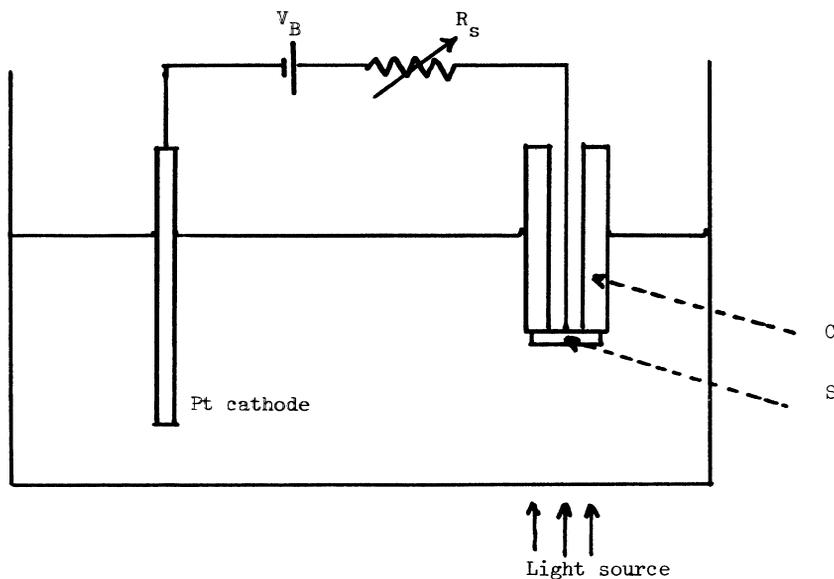


FIGURE 2 Experimental set up for anodic oxidation

$V_B$  – bias supply.  
 $R_s$  – series resistance.  
 $C$  – capillary tube carrying conductor to ohmic contact on back of semiconductor slice.  
 $S$  – semiconductor slice deposited by suitable wax or photoresist.

externally applied voltage<sup>6</sup> so that the oxide thickness will be much smaller than that predicted by the model outlined below.

The results of Figure 1 can be understood as an oxide growth rate which is proportional to the anodisation current minus an approximately constant dissolution rate. The Kirchhoff loop for the voltages gives the following equation:

$$V_B = IR_s + V_r + \int_0^d E dx + IR_B + V_s \quad (1)$$

where  $V_B$  is the supply voltage,  $I$  the current flowing through the series resistance  $R_s$ ,  $V_r$  the rest potential of the anodisation cell,  $E$  the electric field across the oxide of thickness  $d$ ,  $R_B$  the resistance of the bath, the semiconducting chip and of any other circuit part not included yet, and  $V_s$  is the potential of the space charge layer set up by the negative surface charge introduced above.  $V_s$  could also include any other space charge layer of the semiconductor, such as possible with a non-ohmic back contact. Let us assume that  $V_s = 0$  and  $E$  is constant across the oxide. Particularly the latter point is not always valid. However, as the agreement between a theoretical behaviour based on a constant  $E$  agrees well with the experimental findings when the normal growth into a semiconductor without overlaying

metal films is used, we can argue that this assumption too should be valid. It does however seem to break down with some of the multiple-layer structure cases when probably the ionic charge drifting across the oxide results in a substantial accumulation with strong field distortion, particularly at the change-over of growth from one type of material to the next one. The voltage changes across the oxide-semiconductor-ohmic contact structure observed then are too large to be explained by any Schottky-barrier space charge layer between the overlaying metal and the semiconductor.

Eq. (1) can then be rewritten:

$$V_B - V_r = I(R_s + R_B) + Ed \quad (2)$$

where  $d$  is determined by the total electronic charge used to create the oxide thickness, i.e.:

$$d = A \int_0^t (j - j_d) dt \quad (3)$$

Here,  $A$  is defined as the increase in film thickness per unit charge passed through unit area,  $j$  is the current density passing through the oxidising semiconductor surface up to time  $t$ , and  $j_d$  is the dissolution current density. The differential equation resulting from Eqs. (2) and (3) has the following solution:

$$j = \left[ \frac{V_B - V_r}{(R_s + R_B)S} - j_d \right] e^{-t/\tau} + j_d \quad (4)$$

where

$$\tau = \frac{(R_s + R_B)S}{EA} \quad (5)$$

and  $S$  is the surface area of the semiconductor exposed to the electrolyte. Eq. (4) has been found to fit extremely well with experimental findings except for those cases described above where the constant  $-E$  approximation does not hold any more.

The inverse value of  $E$  is therefore also the value of the thickness of oxide produced per voltage applied. This is a value which is characteristic for a particular material and changes with current density employed for the growth. For GaAs it has for example been found to vary linearly between 23 Å/V and 19 Å/V for low current densities of about 0.01 mA/cm<sup>2</sup> to 15 mA/cm<sup>2</sup> respectively. This can be compared with the classical model of Mott and Cabrera, where the ionic current density  $j_i$  across the oxide is given by

$$j_i = a \exp \left( - \frac{Q - q\lambda E}{kT} \right) \quad (6)$$

with  $a$  being a constant,  $Q$  the activation energy for the drift of ions,  $q$  the ionic charge,  $\lambda$  the average jump distance of the ions from one rest well to the next and  $k$  and  $T$  Boltzmann's constant and the absolute temperature respectively. The significance of  $a$  is described by various authors (see for example <sup>7</sup>).  $a$  contains the density of ions in an energetically favourable position to jump and could possibly be used to derive further useful information on ionic transport across the oxide. The terms of Eq. (6) are primarily given by those ionic species being responsible for the largest contribution to  $j_i$ . As for OH<sup>-</sup> both  $Q$  and  $q$  are small, this equation is only affected by these ions when the current density is very small, i.e. when  $E$  is small. Rewriting Eq. (6), i.e.

$$\ln \frac{j_i}{a} = \frac{q\lambda E}{kT} - \frac{Q}{kT},$$

one finds from a graph of the experimental growth current density on a logarithmic scale as a function of  $E$  (linear scale) that the above indicated experimental dependence of  $E$  does indeed follow this relation (see Figure 15 of <sup>3</sup>).

This form of Eq. (6) shows also that one can expect a behaviour as indicated by Figure 3 if one includes the recently established case of oxide growth

due to OH<sup>-</sup> drift only as described above at the end of the previous chapter. There one sees that the slope is determined by OH<sup>-</sup> ions when  $E$  is small, but that the cations with high  $q$  and  $Q$  are responsible for the larger slope at high  $E$  ranges. Unfortunately detailed experimental results are so far only available for the high-field case.

Provided that a particular material satisfies the above assumptions, especially regarding the constancy of  $E$ , the decay of current as shown by Figure 1 is characteristic of a given material, i.e. measured values of  $E$  and  $A$  of Eq. (5) give evidence on the composition of the material. This is firstly of interest where for example by liquid epitaxy ternary compound semiconductors are produced.  $E$  and  $A$  give easy evidence on the ratio of the materials involved. With caution, this can also be employed to measure interdiffusion of thin films on semiconductors.<sup>8</sup> Here one of course has to be aware that a particular metal might form hardly any oxide electrolytically (e.g. In) possibly due to a very high dissolution rate, whereas a mixture of it with some other material does generate a beautiful oxide (for example InP does generate useful native oxides,<sup>9</sup> in spite of the fact that the Pourbaix diagram<sup>10</sup> for phosphorous does not indicate any area where an oxide formation should occur as all the  $P$  is used to form some solution like H<sub>3</sub>PO<sub>4</sub>).

The growth rate of the oxide (e.g. around 20 Å/Volt for GaAs) and the consumption rate of the material (e.g. 14 Å/V for GaAs) give a clear measure of the thickness of a particular layer. The current decay or voltage increase (depending on whether the constant voltage cum series resistance arrangement is used, or the constant current source) will remain the characteristic function until all the material of a particular layer has been consumed and some new material with a different characteristic function arrives. The change from one type of function to another one is often very marked so that the voltage absorbed by the oxide produced gives a clear indication of both the new oxide thickness and the thickness of the layer consumed.

An estimate of the density of the oxide produced is useful. This is now possible with GaAs-oxide by employing the data available. The total electronic charge  $Q$  per surface area employed to grow an oxide thickness defined by the applied voltage  $V_B$  (using the above quoted growth rate of 20 Å/V) is given by an integration of Eq. (4), i.e.:

$$Q = \frac{V_B}{EA}$$

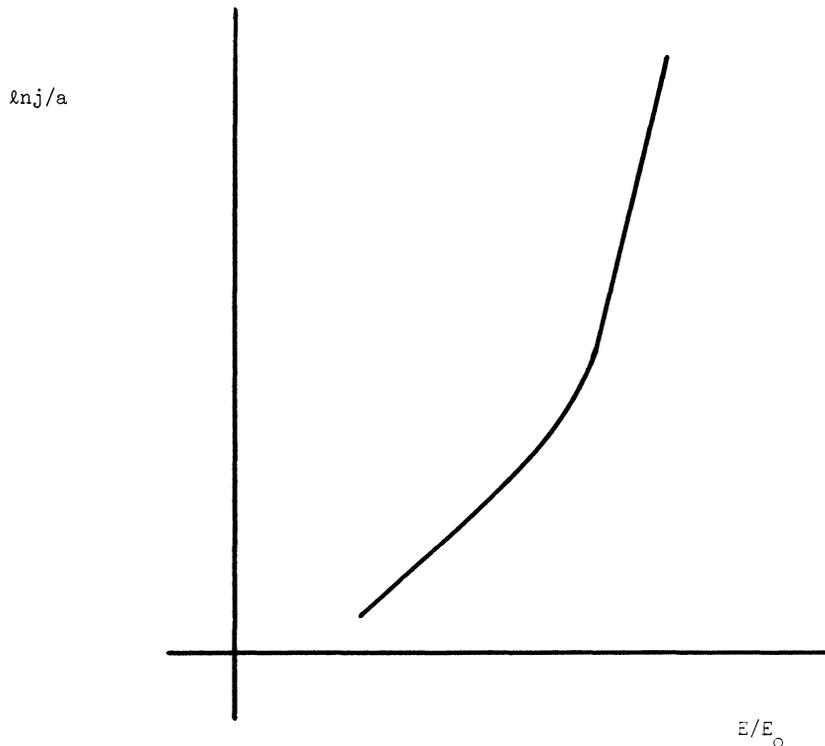


FIGURE 3 Theoretically expected ion current density versus oxide field.  $E_0 = kT/e\lambda$  of Equation (6),  $e$  – electronic charge. For high  $E$ , the larger value of  $q$  for cations causes the current to rise steeper than for small  $E$ .

where  $EA = 3.2 \times 10^2 \text{ cm}^2 \text{ F}^{-1}$  as obtained from such curves as shown in Figure 1. This gives the number of electrons per surface area and per voltage used, namely  $n = 1.65 \times 10^{16} \text{ cm}^{-2} \text{ V}^{-1}$ . For the consumption rate of GaAs,  $14 \text{ \AA/V}$ , there are, on the other hand,  $30.9 \times 10^{14}$  Ga atoms per surface area and per voltage applied, and the same amount of As atoms. Assuming that both types of atoms are triply ionised this would mean that  $1.85 \times 10^{16}$  electrons/cm<sup>2</sup> V were freed, a number which is about 12% higher only than the total number of electrons forming the current causing this anodic process. This small difference is likely to be caused by experimental inaccuracies.

Some useful data was obtained recently by Verplanke and Tijburg on the composition of the native GaAs oxide produced by the glycol solution described here, and on the amount of Ga and As lost into the electrolyte. These results were obtained by radioactive tracer techniques after GaAs was exposed to a neutron flux for two hours so that the material became radioactive. When the anodic growth was undertaken subsequently, the radioactive intensities

of the electrolyte after growth and of an etch solution for partial removal of the native oxide could be measured by a Ge (Li) detector and similar facilities. The recorded activities are then analysed to give the total numbers of Ga and As in these solutions.

It was then found that 25% of Ga and 5% of As is lost into solution. They also found that the As concentration in the oxide is larger than the Ga concentration, except near the surface with the electrolyte where Ga predominates. This seems to indicate that the mobility of Ga ions is higher than those of As so that the latter is ionised by combining with  $\text{OH}^-$  somewhere away from the surface. It is likely that this method can be used to determine the ionic mobilities for the anodic processes considered here.

Using the remaining Ga and As in the oxide and assuming that the oxide consists of  $\text{Ga}_2\text{O}_3$  and  $\text{As}_2\text{O}_3$ , the density of it can be calculated to be  $4.23 \text{ g/cm}^3$ , where the oxide thickness value used for this calculation is relatively reliable as it is based on thickness profile measurements with a Sloan Dektak.

The loss data of Verplanke et al indicates also that the current efficiency for the anodic oxidation is 85% for an average of both cationic species. This is only slightly smaller than the previously published efficiency<sup>3</sup> which was based on very rough estimates of data which was not yet as accurately available then as nowadays.

#### 4. CONCLUSIONS

The anodic oxidation methods available now and the level of understanding of the observed effects make it possible to envisage applications in numerous fields of semiconductor electronics. Further studies are of course needed in order to obtain really optimised conditions, such as a study of the drift mobility for the relevant ionic species.

#### ACKNOWLEDGMENTS

The author is grateful to R. Tijburg of the Philips Research Laboratories in Eindhoven for permission to quote their experimental results before their publication has appeared. Gratitude is also expressed to both the United Kingdom Science Research Council and the European Research Office for financial support for the various projects on anodic oxidation under way in the author's laboratories. Finally he would like to thank those of his research colleagues for numerous useful discussions who are working in this field.

#### REFERENCES

1. H. C. Casey, Jr., "Diffusion in the III-V compound semi-conductors", Chapter 6 in *Atomic Diffusion in Semiconductors*, editor D. Shaw, Plenum Press, London, 1973.
2. R. P. H. Chang, A. K. Sinha., "Plasma oxidation of GaAs", *Appl. Phys. L.*, **29**, July 1976, p. 56.
3. H. Hasegawa, H. L. Hartnagel., "Anodic oxidation of GaAs in mixed solutions of glycol and water", *J. Electrochem. Soc.*, **123**, No. 5, 1976, pp 713-723.
4. B. Bayraktaroglu, E. Kohn, H. L. Hartnagel., "First anodic-oxide GaAs MOSFETs based on easy technological processes", *Electronics Letters*, **12**, No. 2, 1976, pp. 53-54.
5. B. Weiss, E. Kohn, B. Bayraktaroglu, H. L. Hartnagel., "Native oxides on GaAs for MOSFETs - Annealing effects and inversion-layer mobilities", 1976 International Symposium on Gallium Arsenide and Related Compounds, Edinburgh, September 1976, Proc. to be published.
6. A. Colquhoun, H. L. Hartnagel., "Studies of n-type GaAs material properties by anodic current behaviour", *Solid-State Electronics*, **19**, 1976, pp. 819-826.
7. D. A. Vermilyea, *Kinetics of Ion Motion in Anodic Oxide Films*, p. 328, Conference on Non-Crystalline Solids, N.Y. September 1958, Proceedings by J. Wiley, N.Y. 1960, Editor: V. D. Fréchet.
8. A. F. A. B. El-Safti, B. L. Weiss, H. L. Hartnagel., "Analysis of multicomponent thin films on GaAs by anodic processes", *Electronics Letters*, **12**, No. 13, 1976, pp. 322-324.
9. A. Colquhoun, H. L. Hartnagel., "Anodic oxidation of indium phosphide in glycol based solutions", to appear in *Surface Technology*, 1977.
10. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Oxford, Pergamon, 1966.
11. J. C. Verplanke, R. P. Tijburg, "The analysis of anodic oxide films on GaAs and GaP by means of radio active tracer techniques," Private Communication.
12. B. Bayraktaroglu, S. Hannah, H. L. Hartnagel., "Control of Al<sub>2</sub>O<sub>3</sub> position in anodic GaAs native oxide", to appear in *J. Electrochem. Soc.*, 1977.
13. B. Bayraktaroglu, S. Hannah, H. L. Hartnagel., "Stable charge storage of MAOS diodes on GaAs by new anodic oxidation", *Electronics Letters*, **13**, No. 2, 1977, pp. 45-46.



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

