Title	Anodic Native Oxidation of GaAs by AGW Process
Author(s)	Hasegawa, Hideki
Citation	北海道大學工學部研究報告, 79, 79-88

北海道大学工学部研究報告
第 79 号（昭和 51 年）

Bulletin of the Faculty of Engineering,
Hokkaido University, No. 79 (1976)

Anodic Native Oxidation of GaAs by AGW Process

Hideki HASEGAWA*

(Received September 30, 1975)

Abstract

A new and promising method of native oxdation of GaAs is described. It is an anodic oxidation in mixed solutions of glycol and water (AGW process). As compared with proviouses processes, the new process has the advantage of substantially improved stability against impurities in the electrolyte which enables one to anodize GaAs at moderate current density levels of about 1 mA/cm^2 in a very stable and reproducible way. The process also gives films of higher qualitles. Major improvements in the oxide properties are increased imperviousness against metals, a 10^4–10^5 times increase of the resistivity of the oxide with 60–100% increase of breakdown field strength, and increase in the maximum thickness obtainable at room temperature. The details of the process are presented together with the relevant process equations and data. Factors which affect the uniform and reproducible oxidation are briefly discussed.

The as-grown oxide has excellent dielectric properties. Interface properties of MOS capacitors using the anodic oxide are also presented. A suitable post-growth annealing results in dramatic improvements of the interface properties with large reduction of C-V hysteresis, frequency dispersion of accumulation capacitance and fast interface state density.

1. Introduction

As has been fully demonstrated in the tremendous success of the Si-SiO system, availability of a suitable oxidation process is closely related to final utility of a semiconductor material. Surface passivation of devides, MOS type applications from the simple metallization isolation to construction of sophisticated active devices and charge transfer devices, and various processing applications such as masks for selective diffusion are three major types of applications of the semiconductor-oxide system. Ingenious combination of these applications is indeed the heart of the modern silicon planar integrated device technology. With the recent successful developments of GaAs microwave and optoelectronic devices whose performance are not readily available with silicon, an urgent need is now emerging for the full exploitation of planar device concepts to GaAs device families. However, GaAs has been known to be a difficult material to form insulators of acceptable qualities on it. The conventional techniques such as high-temperature thermal oxidation, and deposition of various oxides or nitrides by various CVD techniques are usually unsatisfactory, resulting in the formation of porous films, poor adhesion, poor electronic properties of the interface etc.[1-5] This is one of the important reasons why most of the advanced GaAs devices still stay technologically at the

---

* 電気工学科，電気物性工学講座
* Department of Electrical Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Japan.

stage of " mesa transistor."

The pressnt report is concerned with a new and promising method of native oxidation of GaAs. It is an anodic oxidation process in mixed solutions of glycol and water (AGW process). Although the anodic oxidation has not found a keen practical interest in the Si device technology, such a technique has been known to be very useful among certain metals. Application of anodic means to GaAs technology has a particular advantage in that it can be carried out at low temperatures (room temperature), which can solve the major difficulty associated with the native oxidation of GaAs by conventional means, i. e., the thermal instability of GaAs and its native oxide at elevated temperatures. In fact, the only way known so far to form glassy native oxide with a respectable thickness and low leakage current is the anodic oxidation in the aqueous H_2O_2 solution(6), and that in the solution of N-methylacetamide(7). However, these previous anodic processes involve unfortunately certain process difficulties which would make their practical exploitation rather difficult. On the other hand, the present AGW process can solve these difficulties completely, resulting in a stable, reliable and reproducible oxidation. The process details, comparison with the previous schemes and various properties of the oxides will be presented in this report. A brief description of the process has already been given elsewhere(8,9). It has also been found that the electronic properties of GaAs-oxide interface can be dramatically improved by a suitable post-growth annealing(10,11).

2. AGW Process

2.1 Electrolyte

The general formula of the AGW eiectrolyte is a mixture of (1) glycol (diol or more generally polyhydric alcohol), (2) water and (3) a suitable acid, base or salt. A detailed analysis shows(12) the role of each component as follows: The role of the water is that of the basic anodic oxidant of GaAs. The role of the component (3) is to establish a suitable ionic conduction in the electrolyte. A careful choice must therefore be made for (3) so that no disastrous effect on the oxide growth such as strong oxide dissolution etc. is introduced. For instance, HCl enhances dissolution in a quite substantial manner. The role of the glycol is to stabilize the process. Anodization by an aqueous solution containing components (2) and (3) (AAS process) is possible under conditions of high purity and carefully controlled pH, but it tends to be extremely irreproducibe and results in films of poor qualities with pit formation. The essentil point of the AGW process is that the introduction of a large amount of glycol into the electrolyte stabilizes the whole process and ensures reproducible growth of uniform and dense films. The reason for such a stabilization can be explained on the basis of the fundamental electrochemical processes at the GaAs anode(12), involving electrochemical active-passive transition(13) and simultaneous oxide dissolution during growth. The common features of various AAS electrolytes are a high limiting current density for the active-passive transition and a high film dissolution rate during growth. By the introduction of a fairly large amount of glycol to the AAS system, the limiting current density and oxide dissolution rate are both greatly reduced, and the process becomes extremery stable.

Empirical optimum bath coditions have been established for a particular type of AGW electrolyte which is a mixture of (1) propylene glycol and (2) 3% aqueous solution of tartaric acid buffered with NH_4OH. In such a case, a broad optimum lies at a pH level of the acid solution of 6.2 (adjusted before mixing with glycol) and the volume mixing ratio of glycol to acid selution of 2–4. The data presented in this report are concerned with such an optimum bath.

2.2 Growth Mode

Anodization can be done in either a constant-voltage or a constant-current mode. If the initial current density is above the limiting current density for the active-passive transition which is typically $0.1\ \mathrm{mA/cm^2}$ for the AGW bath, the growth will start after the passage of the passivation time t_p. Fig. 1 shows experimentally observed passivation time vs. the initial current density. The measurement was done on p-GaAs samples withe (100) orientation and a carrier density of $2.2\times10^{16}\ \mathrm{cm^{-3}}$. If the above condition concerning the initial current density is not satisfied, the GaAs anode stays in the active region, and the anodic dissolution will continue. The experiments have revealed that the anodic dissolution of GaAs is generally a nonuniform one, apparently having higher dissolution rates at mechanically damaged parts and edges, producing sharp ditches at the waxed

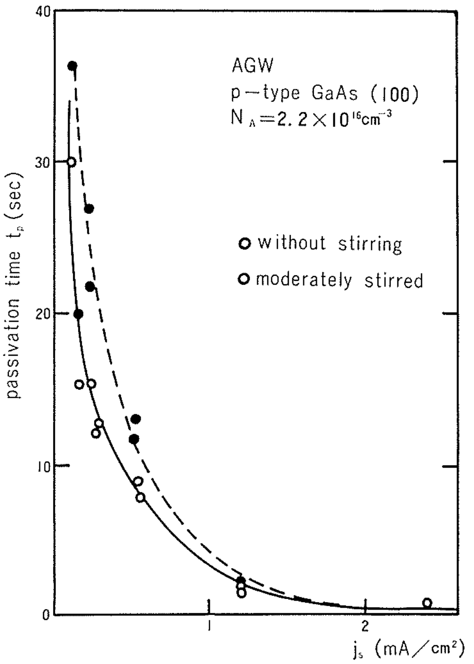

Fig. 1 Observed passivation time t_p vs. initial cnrrent density j_s

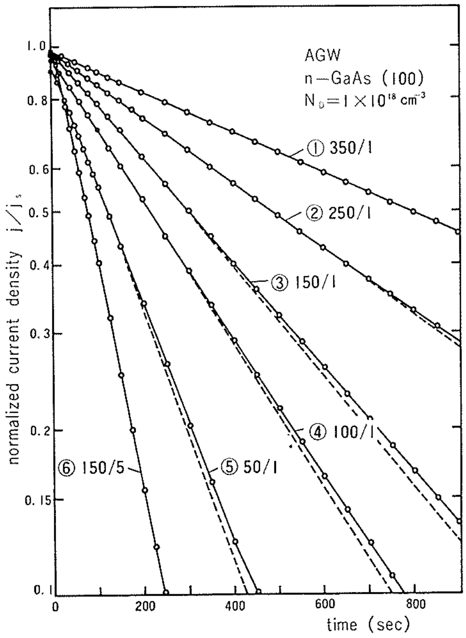

Fig. 2 Plot of currnt density vs. time for AGW prcess. Parameter is V_a (volt)/j_s (mA/cm²)

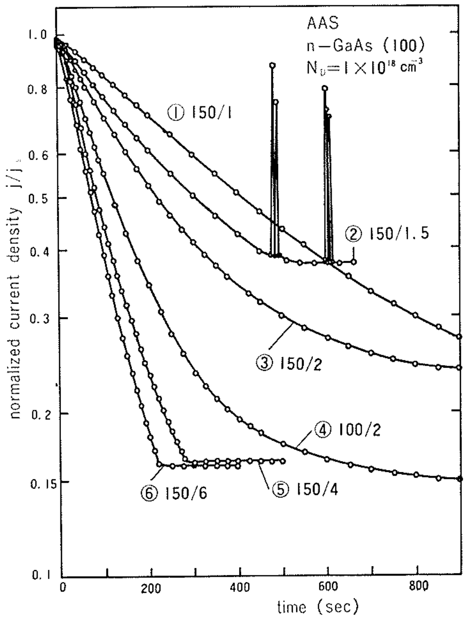

Fig. 3 Plot of current density vs. time for AAS process. Parameter is V_a (volt)/j_s (mA/cm²)

boundary and leaving characteristic pits and lines on the surfaces.

For practical purposes, the constant-voltage mode is easier to employ than the constant-current mode. However, the initial current in the former case is basically limited by the bath resistance, and therefore could be very large. This implies a very rapid growth at the initial stage which can lead to growth of loose oxide and premature electrical breakdown in the oxide during growth. A good compromise can be obtained by inserting an external series resistor R_s into the circuit. In such a case, the growth is essentially exponential where the time costant is determined by R_s. The external circuit conditions can be specified by the source voltage V_a and the short-circuit current density $j_s = V_a/r_s$ where r_s denotes the series resistance per unit area of the anode given by R_sS with S being the area. The relevant process equations are given apporoximately as follows.

$$j=(j_0-j_d)\exp\left(-\frac{t-t_p}{\tau_f}\right)+j_d \tag{1}$$

where

j : anodization current density

t : anodization time

$\tau_f=\dfrac{r_s+r_b}{E_{ox}A}$: formation time constant (2)

A : formation rate defined here as the increase in film thickness per unit charge passed through unit area

E_{ox} : the quasi-steady state field in the oxide

r_b : bath resistance per unit area of the anode

$j_0=j_s\dfrac{1-(V_r/V_a)}{1+(r_b/r_s)}$: the initial current density

V_r : rest potential of the anodization cell

$j_d=\dfrac{1}{A}f_d$: equivalent current desity correspondig to the film dissolution rate f_d

The corresponding thickness of the film is given by

$$x=x_\infty\left[1-\exp\left(-\frac{t-t_p}{\tau_f}\right)\right] \tag{3}$$

where x_∞ is the film thickness in the steady state and is given by

$$x_\infty=\frac{1}{E_{ox}}(V_a-V_r)\left(1-\frac{j_d}{j_0}\right) \tag{4}$$

These equations are only approximate because they are based on a simle Faradyic analysis where development of a quasi-steady-state field in the oxide is assumed, and the dependecy of that field on the current density is ignored. However, the experiments have shown that they describe the general behavior of the process reasonably well. The experimentally observed behavior of the current density is shown in Fig. 2. In the figure, the observed small deviation from the exponential lines (dashed lines) is caused by film dissolution, and when the anodization is carried out for longer periods, this deviation finally leads to constant steady-state currents, which is consistent with Equation (1). A similar set of curves are shown in Fig. 3 for the AAS process using an aqueous solution of 3% tartaric acid buffered by NH_4OH to pH = 6.2 for comparison. One can see that the AGW process behaves in a much simpler, more regular and reproducible manner. The anomalous behavior of the curvers ⑤ and ⑥ in the AAS case has been identified as a premature electrical breakdown in the oxide. The current spikes on curve ② in the AAS case correspond to pit formation. The values of f_d in the above AAS system 1–3 Å/sec, whereas that of the AGW bath is typically 4–6 ×

Table 1 Parameters for AGW process for GaAs cathode meterial: platinum

coating ratio (oxide thickness divided by GaAs consumed)	1.5
formation rate A (at j=1 mA/cm^2)	6.4×10^{-5} cm^3/coulomb
oxide field E_{ox} (at j=1 mA/cm^2)	5.05×10^6 V/cm
current efficiency	90%

10^{-2} Å/sec.

The relevant process equations for the constant-current mode are as follows:

$$V=AE_{ox}(j-j_d)(t-t_p)+V_r+r_b j \tag{5}$$

$$x=A(j-j_d)(t-t_p) \tag{6}$$

where V is the cell voltage.

The values of the important parameters of the process are summarized in Table 1 for the AGW process. For the estimation of current efficiency, the oxide was assumed to be an amorphous mixture of Ga_2O_3 and As_2O_3 on the basis of the analysis of a similar oxide[14].

2.3 Growth Rate

For monitoring and control of the process, the cell voltage provides a good reference which is related to the oxide producing overpotential, and therefore to the thickness of the grown oxide through the thickness-voltage rate constant. The thickness of the grown oxide layers is plotted vs. the overpotential in Fig. 4. Two different ways of the exponential growth are employed here, both being started from around $j_s=1$ mA/cm^2. In the CASE A, the process is terminated at the final current desity 0.1–0.3 mA/cm^2, but, in CASE B, it is terminated around 0.01 mA/cm^2. Both cases give good proportionality between thickness and the overpotential with the rates of 21 Å/V for CASE A and 23 Å/V for CASE B.

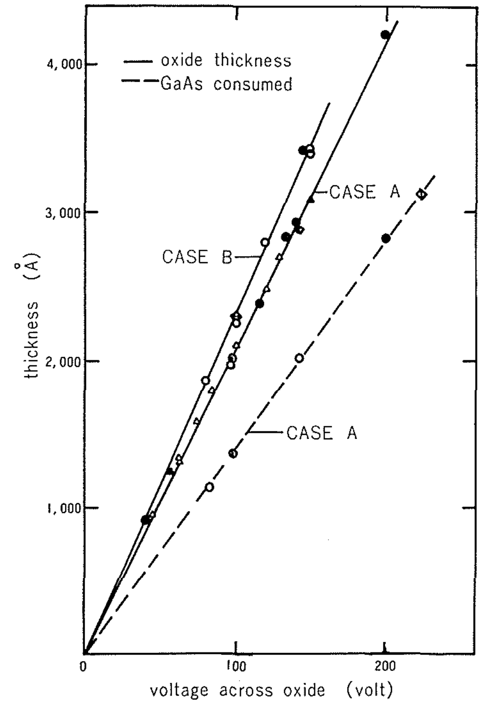

Fig. 4 Thickness-voltage relationship

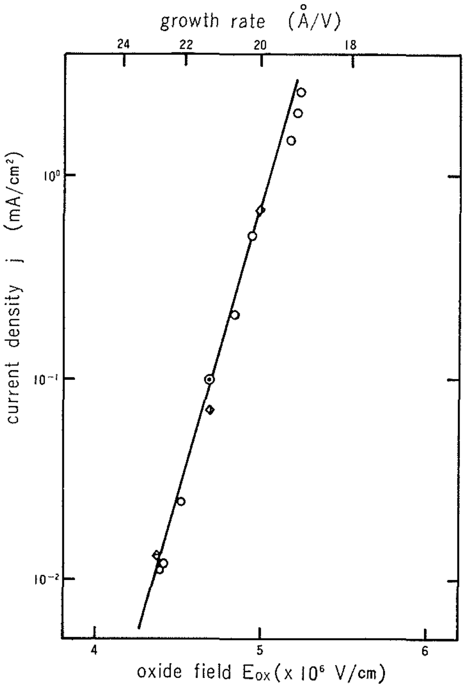

Fig. 5 Observed steady-state current density-oxide field relation

The result also clearly shows that the rate constant is a function of the current density. On the basis of a detailed analysis, the relationship between the steady-state current density and the oxide field shown in Fig. 5 has been obtained. This gives the following empirical formula for the rate constant.

$$\text{rate constant}=\frac{19.8}{1+0.069\log_{10} j}\ \text{Å/V} \tag{7}$$

where the steady-state current density j must be expressed in mA/cm^2. The above observation is obviously consistent with the theory of ionic transport[15], and, in particular, Equation (3) corresponds to a simple Mott-Cabrera type relation. It also explains why different values of rate ranging from 18 Å/V to 22 Å/V were reported in a rather confusing way in the past[6,7,17,18,21]. The amount of GaAs consumed is also shown for CASE A of growth in Fig. 4, and the average consumption rate is 14 Å/V.

2.4 Factors Relevant to Uniform and Reproducible Oxidation

Although the AGW process is potentially stable and reproducible, necessary precautions must be made to realize such a potentiality. Important factors are the sufficient illumination of the anode in the case of oxidation of n-type samples, careful coverage of sample edges and a moderate stirring of the electrolyte. Cleaning of the surface to the "pre-epitaxy" level prior to oxidation is also important.

The reason why a sufficient illumination is necessary for the oxidation of n-type samples is related to the fact that the carriers responsible for the reaction at the anode are holes. Since the electrolyte-semiconductor interface is basically a Schottky junction, supply of holes from the reverse-biased depletion layer in the semiconductor to the interface can limit the rate of the anodic reaction at the n-type anode. Such supply of minority carriers can be made by thermal generation, impact inoization under a high field or photo-excitation under illumination. However, if one relies on the first two means of supply, the resultant process will be severely carrier-concentration-dependent and unpredictable. It will also result in a non-uniform oxidation because a uniform supply of carriers by such means is difficult. The simplest sulution is sufficient illumination to avoid the situation where the hole supply is the rate limiting factor of the total process.

Exposure of the sample edges can also be a cause of quantitative irreproducibility. Its effects are, generally, an increase in the passivation time with a very gradual transition, an increase in the formation time constant, an increase in the rate of GaAs consumption (caused by the slow transition), generation of fluctuation in the anodization current, and reduction in the breakdown voltage of oxide during growth.

After the necessary precautions outlined above are taken, the process becomes very stable and reproducible. Within the range of experiments which involves n- and p-type samples with a carrier concentration of 10^{14}–10^{18} cm^{-3} and orientations of (111), $(\bar{1}\bar{1}\bar{1})$ and (100), no dependence of the process behavior either on the carrier concentration or on the orientation has been observed.

2.5 Comparison with Other Anodic Oxidation Processes

Anodic oxidation of GaAs was first reported by Revesz and Zaininger in 1963[16], but resulted in a severly pitted surface. Dell'Oca, Yan and Young[17] and Harvey and Kruger[18] also reported anodization in various aqueous electrolytes with limited success. Growth of uniform films with low conductivity was first reported by Logan, Schwartz and Sundburg in 1973[6], where a constant-voltage anodization in an aqueous solution of H_2O_2 was used. Various applications have also been suggested based on this encouraging success, which include masks for mesa-etching[6)] and selective Zn-diffusion[16)] and controlled wafer thinning for MESFET's[20)]. More recently, another successful electrolyte was also reported which uses the N-methylacetamide[7)].

The above H_2O_2 scheme has, however, the following serious difficulties: (a) the process lacks stability against impurities and introduction of even 10^{-7} N–10^{-6} N of very common acids such as HCl and HNO_3 into the electrolyte can turn the oxdation into an inhomogeneous anodic dissolution, (b) the grown oxide cannot withstand the vacuum deposition of high-melting point metals such as Au, indicating a lack of imperviousness of the oxide to certain atoms, (c) the grown oxide allows pre-breakdown leakage currents of 10^{-5} to 10^{-7} A/cm^2, which are still rather high as a proper dielectric, (d) reliable growth is limited below 3000 Å because of the onset of anomalous growth which is identified later as the breakdown of the oxide during growth[21)]. On the other hand, very little has been reported on the properties of the oxide produced in the electrolyte containing N-methylacetamide except that it is uniform. The maximum thickness available seems further limited to a lower value than that of the H_2O_2 case, owing to the start of anomalous behavior of the cell voltage at as low as 45 V. Bath conditions require also critical adjustments.

In contrast, the present AGW process can solve the above various problems completely. A systematic study has shown that the process only starts to be affected by the contamination level of 10^{-3} N of HCl or HNO_3, where it still produces a fairly uniform oxide rather than turning into anodic dissolution. The as-grown oxide can with stand Au, Ag or Al deposition in vacuum. The resistivity of the as-grown oxide is 10^4–10^5 times larger than that in the H_2O_2 case with a 60% to 100% increase of the breakdown field strength. The maximum thickness obtained so far at room temperature is 7200 Å with the application of 350 V. The bath conditions have a very broad optimum, and do not require any servere adjustment of pH etc.

3. Properties of Oxide Films

A study of the oxide surface with a scanning electron microscope confirmed that it is smooth and featureless. A high-energy electron diffraction study showed that the oxide has an amorphous glassy structure. Electron microprobe analysis indicated that the ratio of numbers of Ga and As atoms in the grown film is unity on the average.

The chemical properties of the as-grown oxides are similar to those produced by the H_2O_2 electrolyte[6)]. It dissolves into most of the commonly used acids and base solutions except concentrated nitric acid. It is insoluble to most of the commonly used organic solvents such as ethanol, methanol, isopropanol, acetone, trichloroethylene etc., and is also insoluble to halogen-alcohol solutions (such as Br-methanol) which are known to be important etchants of GaAs. It is slowly attacked by hot water.

As-grown oxides have excellent dielectric properties. The breakdown field is 5–6 × 10^6 V/cm, and the prebreakdown leakage current density is 10^{-11} to 10^{-9} A/cm^2. The corresponding specific resistivity ranges from 10^{14} to 10^{16} ohm-cm. The relative permittivity measured at 1 MHz is 7–8.

The as-grown oxide films show a regular occurence of intense interference

Table 2 Interference colours of anodic native oxide of GaAs condition: observed perpendicularly under fluorescent light

thickness Å	colour
500	brown
800	dark violet
1000	royal blue
1300	light blue
1600	light green
1700	yellow
1800	gold
2200	red purple
2400	dark blue
2700	green

Table 3 Interface properties improved by annealing in H_2 gas

annealing conditions	6 hours at 300°C
field-induced hysteresis in terms of effective flat-band voltage shift	below 400 mV for applied field of 1×10^6 V/cm
frequency dispersion of accumulation layer capacitance	change over the frequency range of 100 Hz-1 MHz is below 1%
fast interface state density	$1\text{-}2 \times 10^{11}$ cm^{-2} eV^{-1} near the midgap

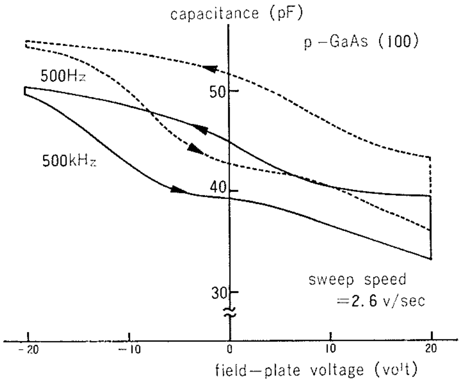

Fig. 6 C-V plot of MOS capacitor for as-grown oxide

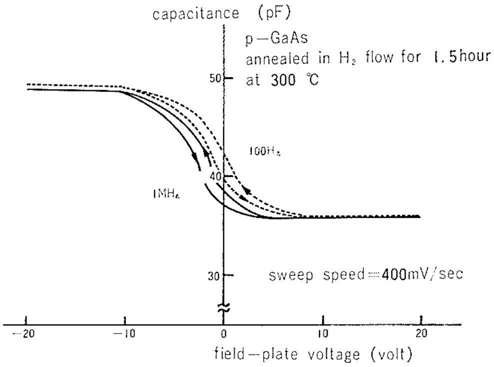

Fig. 7 C-V plot for annealed MOS capacitor

colours which corresponds to the refractive index of 1.8. Although no detailed ellipsometric measurement has been done, its change with the growth the conditions seems to be very small in contrast to the observed fairly large chage in the growth rate constant. Some data concerning the interference colours are listed in Table 2.

The electronic properties of the semiconductor-insulator interface can be studied by the C-V measurements of the MOS capacitors at various frequencies. For the rapid dynamic assessment of the interface properties, an automatic C-V plotting system was specifically developed, which can automaticatically measure the C-V characteristics for a frequency range from 100 Hz to 2.5 MHz and for a sweep speed range of the field-plate voltage of 10 mV/sec.-5 V/sec.[22]

A typical C-V plot of the MOS capacitor formed on an as-grown oxide is shown Fig. 6. The GaAs wafer is of p-type with the carrier concentration of 1.4×10^{17} cm^{-3} and (100) orientation. The field plate is Al with an area of 1.4×

10^{-3} cm^2. The oxide thickness is 1850 Å. This result shows the presence of (1) a large field-induced hysteresis at room temperature, (2) large frequency dispersion of the accumulation capacitance at low frequencies and (3) a high density of fast interface states. All these features are known to be common in the MOS capacitors with deposited oxides or nitrides[2-4, 23], although they are somewhat less pronounced in the present case of the anodic native oxide.

However, it has been found that these inferior interface properties indicating the presence of a large number of traps, can be dramatically improved by the application of annealing in the H_2 flow[10, 11]. Fig. 7 shows the effect of a short time, relatively low-temperature annealing applied to the same oxide as shown in Fig. 6. The hysteresis has been reduced by a factor of 15 in terms of the effective flat-band voltage shift which roughly means a reduction of the slow trap density by the same factor. The frequency dispersion is almost reduced to zero. The best results so far obtained by a longer annealing time at the experimentally found optimum temperature of annealing of 300°C is summarized in Table 3. As far as the author knows, these are the best results reported in the literature on GaAs MOS capacitors. The improvement of interface properties by annealing as reported here makes, in fact, a sharp contrast to previous reports on deposited insuators where annealing has been found almost ineffective. This seems to suggest the importance of having a ' native ' oxide in order to obtain a natural and less defective interface structure.

4. Conclusions

A new promising method of native oxidation of GaAs is presented with the process details and various oxide properties. Further work still seems to be necessary to establish the utility of such a process and the resulting oxide. One of the important research direction will be the enhancement of thermal stability of the oxide in view of the processing applications. Further improvements of interface properties are also required to bring them up to the levels of the Si–SiO_2 system.

Acknowledgement

Most of the work reported here was done at the Department of Electrical and Electronic Engineering, the University of Newcastle upon Tyne, England, where the author stayed on leave of absence from this university. The author would like to express his sincere thanks to Professor H. Hartnagel for his collaboration.

References

1) Rubenstein, M.: J. Electrochem Soc. 113 (1966), p. 540.
2) Foster, J. E. and Schwartsz, J. M.: J. Electrochem Soc. 117 (1970), p. 1410.
3) Cooper, J. A., Ward E. R. and Schwartz, R. J.: Solid-State Electron 15 (1972), p. 1219.
4) Itoh T. and Sakai, Y.: Solid-State Electron. 17 (1974), p. 1219.
5) Baliga, B. J. and Ghandhi, S. K.: IEEE Trans. Electron Devices ED-21 (1974), p. 410.
6) Logan, R. A., Schwartz B. and Sundburg, W. J.: J. Electrochem Soc. 120 (1973), p. 1385.
7) Müller, H., Eisen F. H. and Mayer, J. W.: J. Electrochem Soc. 122 (1975), p. 651.
8) Hasegawa, H., Forward, K. and Hartnagel, H.: Electron. Lett. 11 (1975), p. 53.
9) Hasegawa, H., Forward, K. and Hartnagel, H.: presented at 3rd Int. Conf. of Thin Films, Budapest, Hungry, August 1975, abstract p. 19.

10) Hasegawa, H., Forward, K. and Hartnagel, H.: Appl. Phys. Lett. 26 (1975), p. 567.
11) Hasegawa, H. and Hartnagel, H.: presented at 3rd European Workshop on Microwave Active Semiconductor Devices, Ronneby, Sweden, May 1975.
12) Hasegawa, H. and Hartnagel, H.: to be presented at Symposium of Electrochemical Techniques for Electronic Device Fabrication, The Dallas Meeting of The Electrochemical Socienty, October, 1975.
13) Bockris, J. O'M. (Editor): "Modern Aspects of Electrochemistry No. 2 (Butterworths London 1959)", p. 262.
14) Feldam, L. C., Poate, J. M., Ermanis, F., and Schwartz B.: Proc. of Int. Conf. on Ion Beam Surface Layer Analysis, Yorktown Heights, N. Y., (1973).
15) Bockris, J. O'M. (Editor): "Modern Aspects of Electrochemistry No. 4 (Butterworths London 1966)", p. 176.
16) Revesz, A. G. and Zaininger, K. H.: J. American Ceramis Soc., 118 (1963) p. 606.
17) Dell'Oca, C. J., Yan G. and Young, L.: J. Electrochem Soc., 118 (1971) p. 89.
18) Harvey, W. W. and Kruger, J.: Electrochimica Acta, 16 (1971) p. 2017.
19) Spitzer, S. M., Schwartz, B. and Weigle, G. D.: J. Electrochem. Soc. 121 (1974), p. 820.
20) Rode, D. L., Schwartz, B. and DiLorenzo, J. V.: Solid-State Electron. 17 (1974), p. 1119.
21) Spitzer, S. M., Schwartz, B. and Weigle, G. D.: J. Electrochem. Soc. 122 (1975), p. 397.
22) Forward, K., Hasegawa, H. and Hartnagel, H.: J. Phys. E, 8 (1975), p. 487.
23) Kern, W. and White, J. P.: RCA Review, 31 (1970), p. 1219.