

B-5-8

Anodic Oxidation and MOS Devices of GaAs and GaP

T. Ikoma, H. Tokuda, H. Yokomizo and Y. Adachi

Institute of Industrial Science, University of Tokyo

Roppongi, Minato-ku, Tokyo, Japan

A good insulating film is desired for applications to MOS devices and surface passivation of GaAs and GaP. A good insulating film has to possess high resistivity, high breakdown field, low interface state density, low trap density, chemical stability, and effectiveness in stopping an ion migration. One of the candidates is the native oxide that can be grown by a low temperature process. Revesz and Zaininger first reported the experimental results on the anodic oxidation of GaAs<sup>(1)</sup> We have reported some basic results on the properties of oxide films and MOS C-V curves of GaP and GaAs.<sup>(2)(3)</sup> This paper describes mainly the annealing effect on electrical and chemical properties of the anodic oxides on GaAs and GaP, as well as some characteristics of MOS devices.

1) Oxidation and annealing processes: The wafers cut from n-GaP (100) and (111)  $n=10^{17}-10^{18} \text{ cm}^{-3}$ , n-GaAs (100) and (111)  $n=10^{16}-10^{18} \text{ cm}^{-3}$ , p-GaAs (100)  $p=10^{17} \text{ cm}^{-3}$  and epitaxial n-GaAsP (100)  $n=10^{17} \text{ cm}^{-3}$  were oxidized in the electrolytes of  $\text{H}_2\text{O}_2$  (30%) +  $\text{H}_3\text{PO}_4$  with  $\text{PH}=2.0$  (HP solution) and/or tartaric acid+propylene glycol+ $\text{NH}_4\text{OH}$  with  $\text{PH}=7.0$  (TP solution). The samples were annealed at various conditions; from 220 C to 600 C in air,  $\text{H}_2$ ,  $\text{N}_2$ , or Ar gases for 2 hours after oxidation. The chemical and electrical properties were examined before and after annealing.

2) Electrical properties: The typical change of the current against voltage curves is shown in Fig.1 after various annealing conditions for GaAs. The resistivity of the film is highest after 220 C annealing. By raising the annealing temperature, the leakage current becomes large. The improvement of the resistivity after annealing at 220 C in air will be due to the vapourization of water which was involved during the oxidation<sup>(4)</sup>

The increase of leakage current at higher temperature annealing will be due to the change of the compositions. As reported by Spitzer et al.<sup>(5)</sup> high temperature annealing changes the as-grown oxide to  $\beta\text{-Ga}_2\text{O}_3$  which is poly-crystallized. The breakdown electric field of the film on GaAs decreased by raising the annealing temperature from  $5.0 \times 10^6 \text{ V/cm}$  to  $1.6 \times 10^6 \text{ V/cm}$ . 3) Chemical properties: The compositions of the films were measured by Auger and XMA. The distribution are shown in Fig.2, which is for the film after annealed at 220 C in air.

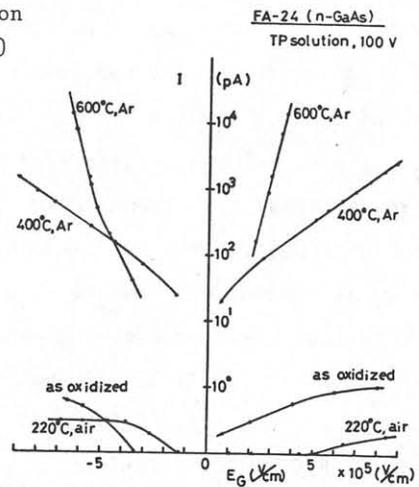


Fig.1 Current vs electric field at various annealing conditions.

The transition region is narrower than the thermally oxidized film. The films were tested in acids and basics. The results are summarized in Table 1. After annealing at 600 C the films become insoluble in all acids except in HF, this also suggests the formation of  $Ga_2O_3$ . The details of the analysis of compositions after annealing will be discussed.

4) C-V and G-V curves: We already reported the C-V and G-V characteristics and their illumination effect of GaP MOS diode.<sup>(2)</sup> These curves are favorably compared with the calculated curves. In the calculation, it is assumed that the flat band voltage was shifted by existence of fixed positive charges of  $1.1 \times 10^{12} \text{ cm}^{-2}$  and injected electrons compensate their positive charges upon applying positive voltage to the metal electrode. The effect of annealing on C-V and G-V curves of GaAs MOS diodes will be presented. One example is shown in Fig.3 and 4.

The frequency dispersion was not improved by annealing at 400 C. The ac conductance decreases in the negative voltage region except after 600 C annealing, while it increases in the positive voltage region. In the presentation, the effect of annealing under various conditions on electrical and chemical properties of the anodic oxides will be presented as well as the characteristics of MOS diodes of GaAs and GaP. The possibility will be discussed on the applications to MOS FETs and optical devices. References

- 1) A.G.Revesz and K.H.Zaininger; J.Am.ceram. Soc.46,606(1963)
- 2) T.Ikoma and H.Yokomizo; to be published in IEEE ED-23 (1976)
- 3) H.Yokomizo et al.; Technical Group Meeting on Solid State Devices, Inst. of Electron. and Comm. Eng. Japan SSD 75-43 (1975)
- 4) B.Schwartz and W.J. Sundburg; J.E.C.S.120,576(1973)
- 5) S.M.Spitzer et al.; J.E.C.S.122,397(1975)

We thank Dr.H.Iida for measurement of AES and XMA.

Fig.4 G-V curves of GaAs MOS diode.

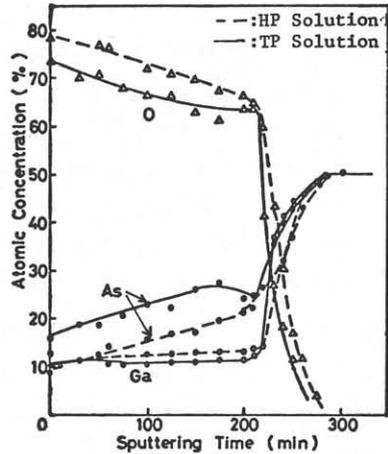


Fig.2 The composition of oxide films

o - dissolved  
 Δ - almost dissolved  
 x - not dissolved

Table 1

etchants	as grown	annealed in N <sub>2</sub>	
		300°C	600°C
HCl	o	o	x
H <sub>2</sub> SO <sub>4</sub>	o	o	x
HNO <sub>3</sub>	o	o	x
H <sub>3</sub> PO <sub>4</sub>	o	Δ	x
CH <sub>3</sub> COOH	o	x	x
HF	o	o	o
NH <sub>4</sub> F	o	Δ	x
NaOH	o	o	x
I <sub>2</sub> +KI+	o	x	x
CH <sub>3</sub> OH	o	x	x
KTFR	o	o	x
Remover	o	o	x

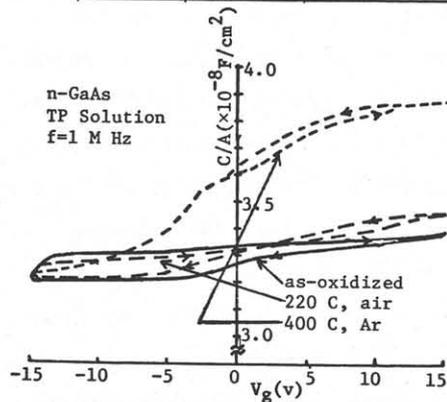


Fig.3 C-V curves of GaAs MOS diode.

