Applied Surface Science 55 (1992) 173–177
North-Holland

applied
surface science

Thermal oxidation of gallium antimonide – surface studies of the substrate and the oxide film

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Received 27 May 1991; accepted for publication 21 October 1991

Native oxide was thermally grown on GaSb by a wet oxidation method. XPS analysis confirmed the formation of both Ga_2O_3 and Sb_2O_3. The surface morphology was studied by scanning electron microscopy. n- and p-type polycrystalline and single-crystal GaSb were used as substrates. n-type substrates showed a more defective oxide surface than the p-type ones. Also substrates with higher carrier concentration showed pit formation during the oxidation process. Prolonged oxidation appreciably deteriorated the GaSb surface. The results were confirmed through C–V measurements of the MOS diodes. SIMS depth profile analysis showed Sb pile up at the oxide/substrate interface.

1. Introduction

Recently GaSb has received renewed interest because of its good IR detection properties useful for fibre optic communication in the wavelength range 1.3–1.7 μm [1]. Since both Ga and Sb do not possess much of a vapour pressure problem, processing of GaSb at high temperature is easier compared to GaAs and InP. Deposition of a thin oxide film on GaSb for MOS device application is a subject of recent research interest. Wilmsen [2] studied the chemical composition and formation of anodic oxides on III–V compound semiconductors. Deposition of native oxide films and oxide–substrate interaction were also reported by Schwartz [3] for III–V compound semiconductors. However, very few reports on thermal oxidation of gallium antimonide are available in the literature [4]. In the present work the surface morphology of thermally grown oxides on both single and polycrystalline GaSb substrates is reported. The nature of the GaSb surface after oxidation was also studied by etching off the oxide layer. The composition of the oxide was confirmed by XPS analysis. SIMS depth profile experiments were conducted to confirm Sb pile-up at the oxide/substrate interface.

2. Experimental details

GaSb samples were obtained from crystals grown by the vertical Bridgman technique in our laboratory [5]. The samples (approximately 5 mm $\times$ 5 mm) were machanically lapped and polished to a mirror finish with Br_2(0.5%)–methanol followed by cleaning with TCE, acetone, methanol and millipore DI water in succession. The samples were finally etched with $1HF:1HNO_3:50H_2O$ for 1 min and repeatedly washed with DI water.

The oxidation was carried out in oxygen atmosphere in the presence of water vapour obtained by bubbling pure oxygen through water kept at 95–97°C. The rate of oxygen flow to the reactor was 18 l/h (6.34×10^{-3} atm) and the optimum temperature of oxidation was 400°C, as determined by preliminary experiments. The temperature of the furnace was maintained with an accuracy of $\pm$0.5°C with the help of a temperature

controller. The XPS analysis and the SIMS depth profile analysis of the oxide films were carried out using an ESCALAB MK-II spectrometer and SIMS apparatus from VG Scientific Instruments Ltd. (UK). The surface morphology of the substrates and the oxides grown was studied using a CAMSCAN MK-II (UK) scanning electron microscope. For investigating the effect of oxidation on the surface of GaSb substrate the oxide was etched off from the surface using 50% HCl. A test run showed that the GaSb surface is not chemically affected by the treatment with 50% HCl.

3. Results and discussion

Native oxides were thermally grown on GaSb. The temperature was varied between 375 and 500°C while the oxygen partial pressure was varied between 5.27×10^{-3} and 9.03×10^{-3} atm. The growth rate showed a linear parabolic kinetic relation with time [4]. Under optimum conditions, e.g. 400°C and 6.34×10^{-3} atm oxygen partial pressure, further growth runs were conducted. X-ray diffraction analysis showed the amorphous nature of the oxide films grown on both n- and p-type GaSb. Fig. 1 shows the XPS analysis of the oxide grown on GaSb. It confirms the formation of both Ga_2O_3 and Sb_2O_3 as the oxide peaks shift towards the higher binding energies relative to gallium and antimony peaks in GaSb [4]. Incorporation of oxygen in the surface was further verified by the presence of an intense oxygen peak which was absent for the bare GaSb substrate. Similar results were reported for anodic oxidation of GaSb [2,3]. The properties of Ga_2O_3 and Sb_2O_3 are presented in table 1.

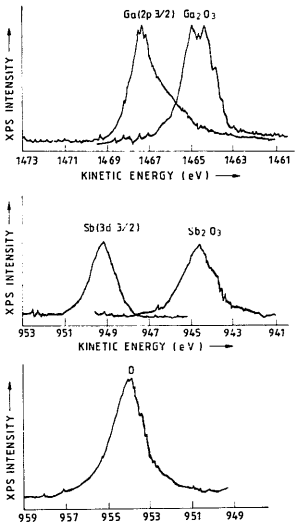

Fig. 1. XPS peaks for gallium, antimony and oxygen on bare and oxidized GaSb.

Fig. 2 shows a SEM picture of the optically polished polycrystalline n-GaSb surface with carrier concentration 1.24×10^{17} cm^{-3} and fig. 3 shows the thermally grown oxide film. The pits observed in fig. 3 are most likely due to non-uni-

Table 1
Properties of Ga_2O_3 and Sb_2O_3

Material	Structure	Melting point (°C)	Density (g/cm^3)	Refractive index	E_g (eV)	ΔG_f (kcal/mol)	ΔH_f (cal/mol)	C_p (cal/mol)
Ga_2O_3	Monoclinic	1715	5.95	1.93	4.7	−238.6	−260.3	22
Sb_2O_3	Cubic	655	5.2	–	6.72	−151.5	−172.05	27.85
	Orthorhombic	–	5.67	2.35	–	−149.7	−169.3	24.23

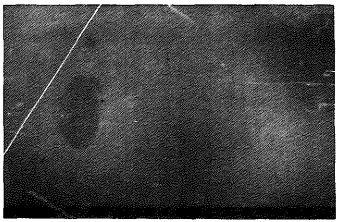

Fig. 2. SEM picture of optically polished n-GaSb surface with $N_D = 1.24 \times 10^{17}$ cm^{-3}.

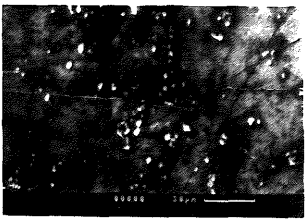

Fig. 4. SEM picture of the oxide film grown on heavily doped n-GaSb with $N_D = 4.7 \times 10^{19}$ cm^{-3}.

formity of the oxide film because of the preferential oxidation of Ga over Sb ($\Delta H_{Ga_2O_3} = -258.5$ kcal/mol and $\Delta H_{Sb_2O_3} = -226$ kcal/mol) and/or adsorption of water vapour. Similar results were also reported by McLaren et al. [7] for native thermal oxide grown on InP. Fig. 4 shows a SEM photograph of the oxide grown on n-poly GaSb with higher carrier concentration (4.7×10^{19} cm^{-3}). The picture indicates the inferior quality of the oxide film. Due to heavy Te doping more Sb are translocated from the lattice sites to the interstitial position and act as active sites for oxidation. This is corroborated by more Sb pile-up at the interface resulting in a high density of pits and a non-uniform oxide film. This is further confirmed by SIMS depth profile analysis (fig. 5). The profile clearly shows the non-stochiometry of the oxide film as we move towards the substrate and a sharp Sb pile-up at the oxide/substrate interface. The results were verified through C–V characteristics of the MOS diodes which deteriorated with higher carrier concentration substrates.

The oxide/GaSb interface composition is tabulated in table 2 [6]. Figs. 6a and 6b show the surfaces of n-poly-GaSb (1.24×10^{17} cm^{-3}) after the oxide film was removed by acid etching, oxidation time being 2 and 4 h, respectively. The surface remains fairly uniform after 2 h oxidation as is evident from fig. 6a. But after 4 h oxidation

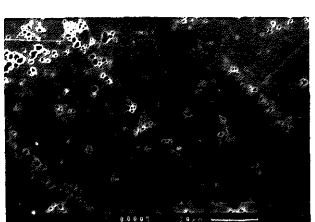

Fig. 3. SEM picture of the oxide film grown on n-GaSb with $N_D = 1.24 \times 10^{17}$ cm^{-3}.

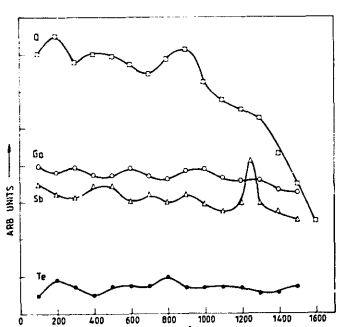

Fig. 5. SIMS depth profile for oxidized GaSb.

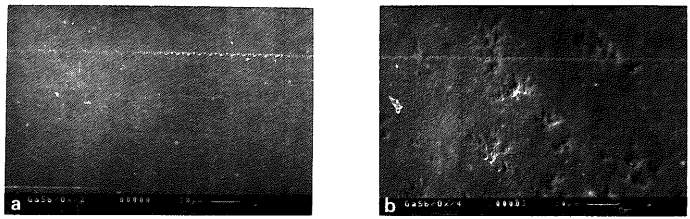

Fig. 6. SEM picture of oxide/substrate interface: (a) after 2 h oxidation and (b) after 4 h oxidation.

pits are visible on the substrate surface (fig. 6b). Table 2 shows that the oxide/GaSb interface is comprised of Ga_2O_3 and elemental Sb after thermal oxidation. During acid etching of the oxide film elemental Sb is also removed from the GaSb surface, leaving behind the pits as observed in the SEM picture. So it can be inferred that more pits are formed with longer time of oxidation.

Fig. 7 shows a SEM picture of the oxide grown on p-type polycrystalline GaSb. The overall oxidation rate is lower than that of n-poly-GaSb (fig. 3). It is well known that the conductivity in p-type GaSb arises due to Ga vacancies in the lattice sites. It is also seen from table 1 that the oxidation rate of Ga is higher than that of Sb. Thus, Ga vacancies in the lattice site of p-GaSb reduce the oxidation rate. It was observed that the oxidation rate of single-crystal p-GaSb was even lower due to the absence of grain boundaries which enhance the oxidation rate of polycrystalline GaSb due to oxygen segregation [8]. Fig. 8 shows a SEM picture of the oxide grown on p-type single-crystal GaSb.

4. Conclusion

During thermal oxidation of n- and p-GaSb the substrate deteriorated with longer time of oxidation due to piling up of elemental Sb at the interface. With GaSb substrate of higher carrier concentration the oxidation rate was higher and the oxide film was non-uniform. The oxide quality was also inferior as was tested by C–V measurements of MOS diodes.

Fig. 7. SEM picture of the oxide film grown on polycrystalline p-GaSb with $N_A = 2.73 \times 10^{17}$ cm^{-3}.

Fig. 8. SEM picture of the oxide film on single-crystal (111) p-GaSb with $N_A = 2.73 \times 10^{17}$ cm^{-3}.

Table 2
Oxide/semiconductor interface composition

Compound	Equilibrium	Thermal oxide	Anodic oxide	Anodic oxide (annealed)
GaSb	Ga_2O_3 + Sb	Ga_2O_3 + Sb	Ga_2O_3 + Sb_2O_3	Ga_2O_3 + Sb

Acknowledgement

The authors thank Dr. U.N. Roy, ex-Research Scholar of the Centre for growing GaSb crystals.

References

[1] Y. Nagao, T. Hariu and Y. Shibata, IEEE Trans. Electron Devices ED-28 (1981) 407.
[2] C.W. Wilmsen, J. Vac. Sci. Technol. 19 (1981) 279.
[3] G.P. Schwartz, Thin Solid Films 103 (1983) 3.
[4] P. Barman, N. Basu and S. Basu, Semicond. Sci. Technol. 6 (1991) 129.
[5] U.N. Roy and S. Basu, Bull. Mater Sci. 13 (1990) 27.
[6] Physics and Chemistry of III–V Compound Semiconductor Interfaces (Plenum, New York, 1985) pp. 406–409.
[7] J.J. McLaren, A. Nelson, K. Geib, R. Gann and C.W. Wilmsen, J. Vac. Sci. Technol. A 1 (1983) 1486.
[8] U.N. Roy and S. Basu, J. Appl. Phys. 65 (1989) 1379.