Liquid phase oxidation for InGaP/GaAs HBT passivation

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Abstract
Native oxide films grown near room temperature by liquid phase oxidation (LPO) on p+-GaAs, n-InGaAs and n-InGaP are investigated. Their applications to heterojunction bipolar transistors (HBTs) are also demonstrated and characterized. With the LPO as surface passivation, the dc current gain $\beta$ of the HBT devices increases sevenfold in low collector current regimes, and it also shows wider collector regimes from $8.3 \times 10^{-11}$ A to 0.1 A. In addition, a larger breakdown voltage and lower surface recombination current can be obtained. This provides the possibility of promising implementations in low-power electronics and communication applications. Comparisons between devices with LPO passivation and those with sulfur treatment on the InGaP/GaAs HBTs are also discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

InGaP/GaAs HBTs have attracted much attention because of their high-speed and high-power applications, which are mainly due to their superior transport properties and lower costs over other microwave devices. Compared with conventional AlGaAs/GaAs HBTs, InGaP/GaAs HBTs have several advantages, such as higher InGaP energy gaps, higher valence-band discontinuity, absence of deep-complex (DX) centres, excellent etching selectivity between InGaP and GaAs and good thermal stability. Because higher densities of surface states and higher speeds of surface recombination in III–V materials are observed, surface passivation becomes one of the key factors in fabricating high-performance electronic and optoelectronic devices. For the III–V material system, passivation is a crucial process for fabricating high-performance electronic and optoelectronics devices. The emitter ledge method has been found to be very effective in reducing the surface recombination current to further enhance the current gain, especially in the low emitter current regime, and improve the noise characteristics [1]. However, suitable control of the ledge layer thickness is crucial. In addition, efforts have been substantially exerted to find a proper method for reducing the GaAs surface states by surface passivations, including a chemical treatment using an (NH₄)₂S solution, and a plasma treatment using H₂ and N₂ [2–5]. The traditional sulfur treatment removes the oxides on the surface to improve the surface states. However, after treatment, there are still some oxides which remain on the surface. Moreover, sulfide is easily evaporated and, hence, the degradation of device performance is expected [6, 7].

Over the past few years, an alternative technique named liquid phase chemical-enhanced oxidation (LPCEO) on GaAs [8–12], AlGaAs [13, 14], InGaP [15], InGaAs [16], InAlAs [16] and so on has been demonstrated. This is a stable, reliable, simple and low-temperature (30–70 °C) technique in growing uniform and smooth native oxide films. In the liquid phase oxidation system, neither an anodic equipment nor an assisting energy source is needed. In this paper, studies on the native oxide on p+-GaAs, n-InGaAs and n-InGaP as well as chemical and electrical applications to the base surface passivation on InGaP/GaAs HBTs without emitter ledge are demonstrated. The surface passivation of p+-GaAs by LPO can effectively reduce the density of the surface
states, resulting in the reduction of the surface recombination speed and in the improvement of the device performance. Moreover, comparisons between InGaP/GaAs HBTs with LPO passivation and those with sulfur treatment are also made.

2. Experimental details

The structure used for the study of the native oxide on p'-GaAs, n-InGaAs and n-InGaP is based on the HBT, as given in figure 1. The epilayers were grown by a low-pressure metal organic chemical vapour deposition (LP-MOCVD) system on a (1 0 0)-oriented semi-insulating (SI) GaAs substrate. It consists of a 600 nm GaAs subcollector layer, a 20 nm In$_{0.51}$Ga$_{0.49}$P etching stop layer, a 750 nm GaAs collector, a 100 nm GaAs base layer, a 40 nm In$_{0.51}$Ga$_{0.49}$P emitter layer, a 130 nm GaAs subemitter, a 45 nm In$_{0.51}$Ga$_{0.49}$P graded layer and a 45 nm In$_{0.51}$Ga$_{0.49}$P cap layer. This design is for the oxidation study as well as for the HBT. The oxidation system is simple and very low in cost because it only consists of a temperature regulator and a pH meter [8]. Using selective etching, the InGaAs capping layer was removed to the InGaP, while the InGaP was also removed to the p'-GaAs. The etching solutions of the GaAs or the InGaAs and InGaP were H$_2$PO$_4$:H$_2$O$_2$:H$_2$O = 1:1:20 (50 Å s$^{-1}$) and H$_3$PO$_4$:HCl = 1:1 (150 Å s$^{-1}$), respectively.

Before oxide growth, the wafers were cleaned in a HF solution with HF:H$_2$O = 1:200 for 1 min to remove the existing oxide and to further ensure a clean surface. After standard cleaning, the GaAs, InGaAs and InGaP samples were immersed into the gallium-ion-contained nitric acid solution to form the oxidized layer. The oxidation system is simple and very low in cost because it only consists of a temperature regulator and a pH meter [8]. Using selective etching, the InGaAs capping layer was removed to the InGaP. The etching solutions of the GaAs or the InGaAs and InGaP were H$_2$PO$_4$:H$_2$O$_2$:H$_2$O = 1:1:20 (50 Å s$^{-1}$) and H$_3$PO$_4$:HCl = 1:1 (150 Å s$^{-1}$), respectively.

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Figure 4. XPS surface profiles for the p+-GaAs (a) Ga-3d and (b) As-3d core levels for the samples.

Figure 5. XPS surface profiles for the n-InGaAs (a) In-3d, (b) Ga-3d and (c) As-3d core levels for the samples.

Figure 6. XPS surface profiles for the n-InGaP (a) Ga-3d, (b) In-3d and (c) P-2p core levels for the samples.
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Figure 7. AFM images of (a) the p+-GaAs and (b) the InGaP samples before and after liquid phase oxidation.

3. Results and discussion

Figure 2 exhibits oxide thickness as a function of the oxidation time at 50 °C without pH control [9] for p+-GaAs, n-InGaAs and n-InGaP. The AES depth profiles of the as-oxidized p+-GaAs and n-InGaAs native oxides exhibiting gallium, arsenic and oxygen from the surface to the inner state are shown in figures 3(a) and (b), respectively. Oxygen is clearly found from the surface to the inner state of the (In)GaAs layer. The oxidation rate of p+-GaAs is less than that of n-GaAs, which is consistent with the results of [10]. The XPS depth profiles of the LPO-grown oxide for In0.49Ga0.51P are shown in figure 3(c).

Although the liquid phase oxidation on the InGaP material has a much slower oxidation rate, it resulted in a thin oxide film (<10 nm) for 1 h as compared to that of the GaAs material.

The XPS spectra of (a) Ga-3d and (b) As-3d core levels for the p+-GaAs native oxide are shown in figure 4. The binding energies for all spectra are calibrated with the reference signals of the as-received samples. The Ga2O3 (20.3 eV) is characterized by chemical analysis with a shift of 1.3 eV higher than the one of Ga and As2O3 (44.3 eV), which has a shift of 3.3 eV higher than the one of As. Based on the analysis results of the oxide films grown by the LPO method, the grown oxide is mainly composed of Ga2O3 and As2O3. Figure 5 shows the XPS surface spectra of the InGaAs for (a) Ga-3d, (b) In-3d and (c) As-3d. The as-received sample was cleaned in a HF solution with HF:H2O = 1:200 for 30 s. It clearly suggests that the oxide film is mostly composed of Ga2O3, As2O3 and indium oxide. Meanwhile, figure 6 shows the XPS surface spectra of InGaP for (a) Ga-3d, (b) In-3d and (c) P-2p. The as-received sample was cleaned in a HF solution with HF:H2O = 1:200 for 30 s. It clearly suggests that the oxide film is mostly composed of InPO4 and Ga oxide.
The oxide film may appear to be etched back in the growth solution after 2 h of oxidation.

The thermal stability of the oxide layer is important in device fabrication because high-temperature processes are usually required. XPS is utilized to analyse the surface chemistry of the oxide films. After 2 h of oxidation, the annealing processes were performed in a furnace, with \( \text{N}_2 \) flowing at different temperatures for 1 min; however, a peak of InPO\(_4\) is still observed. As a result, the InPO\(_4\) probably acts as a capping layer for the entire oxide film to enhance thermal stability [15].

In order to investigate the surface roughness of LPO-grown oxide films, atomic force microscopy (AFM) images are measured. The surface morphology of the p\(^+\)-GaAs layers as-received and with oxide films for 1 h of oxidation is shown in figure 7(a). From these AFM images, a smooth surface with a root mean square (rms) variation of less than 1 nm can be achieved for an oxide thickness of 600 Å. The AFM measurement for InGaP surface roughness is estimated to be 1.1 nm in root mean square value before oxidation and can still be improved to 0.95 nm after oxidation, as shown in figure 7(b). The rough surface is mainly due to the etched surface. Therefore, it implies that the oxide film grown by the LPO method can improve surface roughness, which could be of great benefit to device fabrication.

Figure 8 shows the common-emitter current–voltage (\( I-V \)) characteristics of the HBTs (a) without passivation, (b) with LPO-grown oxide passivation and (c) with sulfur treatment. The emitter area \( A_E \) is 40 × 40 \( \mu \text{m}^2 \). The dc current gain \( \beta \) values of devices (a), (b) and (c) are 66.0, 72.5 and 71.5 at \( I_B = 20 \mu \text{A} \) and the breakdown voltages of \( \sim 12 \, \text{V} \), respectively. Clearly, compared with HBTs without passivation, both \( \beta \) of the HBTs with LPO-grown oxide passivation and with sulfur treatment showed 10% improvement. Compared with those of conventional InGaP/GaAs HBTs, the studied device shows the highest improvement of \( \beta \). The higher \( \beta \) with oxide passivation is attributed to the reduction of the recombination current in the exposed extrinsic base regions by LPO. The common-emitter \( I-V \) characteristics of the devices (a) without passivation, (b) with LPO-grown oxide passivation and (c) with sulfur...
Passivation have a higher $\beta$ recombination current. Moreover, the devices with surface $V_{CB}$ at a lower shows the lowest base current ($2 \times 10^{-5}$ A) at a lower base–emitter voltage.

Figure 9. The devices with oxide passivation have a higher $\beta$ at a lower base–emitter voltage. The maximum sevenfold increase in the current gain at the collector current went down to the nA level which is attributed to the suppression of surface state density, i.e., the surface recombination current is effectively reduced [5]. The results may not be as good as that of the best from the emitter ledge [1]; however, the used method takes the advantages of the simple process.

Figure 11(a) shows the currents as a function of the perimeter to area ratio at different collector current densities of 0.01 and 1 A cm$^{-2}$. The collector currents are almost identical without being affected by the passivation treatment. For the device with sulfur treatment, the typical breakdown voltage of 22.6 V is slightly higher than 21.9 V without passivation at $I = 50 \mu$A. In addition, the device with oxide passivation shows the highest recombination–base–collector breakdown voltage of 23.5 V (as the histogram of the breakdown voltages for 40 specimens with surface passivation is shown in figure 11(b)). This is attributed to the LPO-grown oxide in the base region and the elimination of the sidewall leakage path by the passivation of the native oxide.

Figure 12 shows the inverse dc current gain as a function of the perimeter to area ratio $L/A$ at different collector current densities of 0.01 and 1 A cm$^{-2}$ for the devices without passivation, with LPO-grown oxide and with sulfur treatment. The device with LPO-grown oxide also shows the lowest surface recombination current, while the traditional sulfur treatment eliminates the oxides of the surface and improves the surface states. However, there are still some oxides remaining on the surface, and the sulfide is easily evaporated, which results in the degradation of device performance. In addition, after 48 h, the current gain...
degradation of the HBT with oxide passivation is about 5%, which is much better than the 25% of the sulfur-passivated ones. Thus, the proposed stable and reliable LPO can easily be implemented in device applications.

4. Conclusions

Uniform and reliable native oxide films grown by liquid phase oxidation on the p⁺-GaAs, n-InGaAs and n-InGaP layers near room temperature were investigated. Compared with conventional InGaP/GaAs HBTs without passivation, the HBTs with oxide passivation proposed in this work possess the characteristics of lower recombination current, higher reverse-bias base–collector breakdown voltage and higher dc current gain. The devices with surface passivation by the native oxide increased sevenfold in current gain at low collector current regimes by the reduction of the surface recombination current, compared with those without passivation. Likewise, a better lifetime for passivation as compared to sulfur treatment was demonstrated. Therefore, it is shown that the proposed low-temperature and stable liquid phase oxidation can easily be implemented in device applications.

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