Chemical and electrical characterization of AlGaAs/GaAs heterojunction bipolar transistors treated by electron cyclotron resonance plasmas

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The effects of electron cyclotron resonance (ECR) hydrogen, nitrogen, and ammonia plasma have been studied by x-ray photoelectron spectroscopy. Experimental evidence shows that the ECR hydrogen plasma removes the native oxide on the GaAs surface and recovers the surface order. A mixed nitride-oxide surface layer is formed after nitrogen and ammonia plasma treatments. The appearance of the nitride layer correlates with the passivation of the GaAs surface and the much improved $I$-$V$ characteristics of AlGaAs/GaAs heterojunction bipolar transistors.

The AlGaAs/GaAs heterojunction bipolar transistor (HBT) has been recognized for its potential in ultrahigh-speed digital and microwave analog circuit applications. One of the major limitations of the AlGaAs/GaAs technology is the current gain degradation associated with the scaling of the emitter-base junction size. The current degradation is known to be related to the high surface recombination velocity of GaAs. Several methods have been developed to reduce this recombination current, e.g., using graded base structure or passivating the emitter-base periphery with sulfide treatments. Unfortunately, the graded base introduces unnecessary process complexity and the sulfide treated surface is not stable. Recently, we have reported the first experiment of electron cyclotron resonance (ECR) hydrogen and nitrogen plasma surface passivation of the AlGaAs/GaAs heterojunction bipolar transistor (HBT). As a result of the plasma treatment, the low-current current gain was enhanced by a hundred-fold, and the collector and base current ideality factors were improved. In this letter, we report in situ x-ray photoelectron spectroscopy (XPS) of the surface before and after each ECR plasma step, and the surface spectroscopy is then correlated with the electrical measurements of the HBT. In addition, we present new experimental data with the collector current-voltage characteristics and the junction reverse leakage currents were measured by HP4145B.

The XPS spectrum of the GaAs sample before hydrogen plasma treatment shows a strong oxygen signal, indicating the surface is covered by a native oxide. Expanded spectra of the As2p and Ga2p core levels are shown in Fig. 1. For As bound to GaAs, the As2p core level produces emission at binding energy around 1322 eV. For Ga in GaAs, the Ga2p core level is positioned around 1117 eV.

The experiments were carried out in an ultrahigh vacuum (UHV) system with two independent chambers equipped with a monochromatic Al Kα XPS, a residual gas analyzer (RGA) and a custom made ECR plasma source. The base pressure is 1 $\times$ 10$^{-8}$ and 5 $\times$ 10$^{-10}$ Torr for the processing chamber and the analysis chamber, respectively. The ECR plasma is produced with a 120-W, 2.45-GHz microwave source. A 1.5-in.-diam quartz cell on the processing chamber and the analysis chamber, respectively. The ECR plasma is produced with a 120-W, 2.45-GHz microwave source. A 1.5-in.-diam quartz cell on the electromagnet, allows the microwave power to be absorbed by the gas in an 875-G magnetic field. The processing gas is introduced at the base of the quartz cell, and the typical chamber pressure is 1 $\times$ 10$^{-3}$ and 5 $\times$ 10$^{-4}$ Torr for hydrogen and nitrogen (or ammonia), with a flow rate around 7 sccm. Samples used in our experiment are $Np(n$ AlGaAs/GaAs HBTs with a two-dimensional electron gas (2DEG) emitter. A GaAs wafer is used as a control sample for the XPS surface analysis. The 2DEG-emitter HBT has a high current gain, a low offset voltage, but large leakage currents. Samples are positioned 22 cm from the center of the plasma source. Typical ion energies in the ECR plasma are around 20 eV, and the ion-current density at the sample position is measured using a Faraday cup to be Isat = 0.4 $\mu$m/cm$^2$ for hydrogen with absorbed microwave power of 80 W. The sample may be biased to eliminate either positive or negative particles from being incident on the sample, which allows modification of the reaction conditions. Under the typical XPS data acquisition conditions, the Au 4f/2 peak at 84.0 eV binding energy (BE) has a full width at half-maximum (FWHM) of 1.0 eV. The run-to-run energy position resolution is within ±0.05 eV. The analyzer settings and acquisition time for each run were kept constant in order to make meaningful comparisons of the peak areas, which correspond to the elemental concentrations. Before loading into the UHV system, the samples were cleaned by NH$_3$OH:H$_2$O (1:1) to remove the native oxide. The ECR hydrogen plasma treatment was set for 30 min at 250 °C with a sample bias of —22 V. Half of the hydrogen plasma treated samples were treated with a nitrogen plasma for 10 min and the others were treated with a 10 min ammonia plasma at room temperature. The collector current-voltage characteristics and the junction reverse leakage currents were measured by HP4145B.

The XPS spectrum of the GaAs sample before hydrogen plasma treatment shows a strong oxygen signal, indicating the surface is covered by a native oxide. Expanded spectra of the As2p and Ga2p core levels are shown in Fig. 1. For As bound to GaAs, the As2p core level produces emission at binding energy around 1322 eV. For Ga in GaAs, the Ga2p core level is positioned around 1117 eV. The oxide composed of As$_2$O$_3$ and Ga$_2$O$_3$ is characterized by chemical shifts of 3 and 1 eV toward higher binding energies, respectively. After 30 min of hydrogen plasma processing at 250 °C, the As$_2$O$_3$ signal completely disappeared and the emission intensity of the main peak As2p increased. The oxygen O1s signal decreased, indicating that the hydrogen plasma reduces the As$_2$O$_3$ with subsequent oxygen removal. For Ga, some oxygen signal Ga$_2$O$_3$ is still detectable and the observed intensity increase of the
main peak is larger for Ga\textit{2p} than for As\textit{2p}. These results indicate that oxygen in As\textsubscript{2}O\textsubscript{3} reacts with hydrogen plasma more readily than oxygen in Ga\textsubscript{2}O\textsubscript{3}, and the hydrogen plasma appears to have removed the excess As to re-establish a clean stoichiometric GaAs surface. This is also reflected in a slight decrease of the FWHM of the core levels.

The effect of the nitrogen plasma on the cleaned GaAs surface is plotted in Fig. 1(c). The shoulders in both the As\textit{2p} and the Ga\textit{2p} levels are indications of the formation of a mixed surface nitride-oxide layer. Since a surface layer is formed, the intensity of the core levels signal for GaAs decreases. The observed XPS intensity reduction of the main peak is larger for As\textit{2p} than for Ga\textit{2p}. This result may be interpreted as As dangling bonds saturated by N atoms. The origin of the oxygen is likely to come from the residual moisture sticked on the chamber or the gas roughing line. In addition to baking out the chamber, a liquid nitrogen (LN\textsubscript{2}) cold trap is wrapped around the roughing line to purify the processing gas.

The influence of the ammonia plasma on the cleaned GaAs surface is different from the case of nitrogen plasma treatment. The XPS data are shown in Fig. 2. After the ammonia plasma treatment, a mixed surface nitride-oxide layer is also formed. However, instead of detecting a strong O\textit{1s} peak, we observe a slight increase in the intensity of the oxygen. The shoulders in the As\textit{2p} and Ga\textit{2p} levels are nitride rich. The reduction of the oxygen signal can be explained as follows: during the ammonia plasma processing, both the nitrogen and hydrogen plasma play a role in the reaction. Therefore, when the surface is nitridized, the hydrogen plasma also clean the GaAs surface.

The currents as a function of the emitter junction bias (Gummel plot) of the HBT are plotted in Fig. 3. Before the ECR plasma process, the collector ideality factor is 1.26 and the base current has a large leakage component with an ideality factor of 2.67 at \( V_{bc} \) less than 1.02 V. After the hydrogen and nitrogen ECR treatment, the base current and collector current ideality factors become 1.96 and 1.08, respectively, at \( V_{bc} \) less than 1.08 V, which are improved further to 1.49 and 1.02 by replacing nitrogen with ammonia. These changes are proportional to the ratio of the arsenic nitride to arsenic oxide qualitatively. It is clearly seen that the shunt leakage current is reduced significantly by the ECR plasma. We found that the recombination current associated with the surface states is also reduced effectively. According to Tiwari’s results, surface recombination current has an ideality factor of 2. The ideality factor of the base current density in combination with the bulk and surface recombination components is usually between 1 and 2. The corresponding current gains as a function of the collector current density are shown in Fig. 4. These data are consistent with lower junction recombination for ammonia treated samples. In other words, there appears to be fewer surface states after the ammonia treatment than after the nitrogen treatment. The current-voltage characteristic of the HBT remained the same after ex-

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**FIG. 1.** XPS spectrum of ECR hydrogen, nitrogen plasma treated GaAs(100) surfaces. (a) 50% NH\textsubscript{3}OH clean (1 min), (b) 30 min ECR hydrogen plasma at 250°C, (c) 30 min ECR hydrogen and 10 min nitrogen plasma.

**FIG. 2.** XPS spectrum of ECR hydrogen, ammonia plasma treated GaAs(100) surfaces. (a) 50% NH\textsubscript{3}OH clean (1 min), (b) 30 min ECR hydrogen plasma at 250°C, (c) 30 min ECR hydrogen and 10 min ammonia plasma.

**FIG. 3.** Gummel plot of the HBT before (dotted line) and after the ECR hydrogen and nitrogen plasma (dashed line) and ECR hydrogen and ammonia plasma (solid line).
Exposure to air for a week. Most of the devices degraded after two weeks of storage but it can be recovered with another ECR treatment. It seems that the thin nitride-oxide layer is oxygen permeable. The regrown As₂O₃ appears to be responsible for the device degradation with aging.

In summary, XPS analysis has been carried out on n⁺-GaAs surfaces cleaned by hydrogen, nitrogen, and ammonia ECR plasma. The hydrogen plasma was found to remove the native oxide and recover the surface order. A mixed surface nitride-oxide layer was formed after the nitrogen and ammonia plasma treatments. An improved base current ideality factor of AlGaAs/GaAs HBTs is obtained. The improved device performance is due to the removal of the native oxide and passivation of As atoms on the GaAs surface. When a thicker nitride layer is obtainable, the ECR hydrogen, nitrogen, and ammonia plasma treatments could offer a practical technique for the surface passivation of AlGaAs/GaAs HBTs.

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