Operation and device applications of a valved-phosphorus cracker in solid-source molecular-beam epitaxy

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Solid phosphorus is successfully incorporated into a molecular-beam epitaxy system by a valved-cracker for the growth of phosphorus-based materials. The operating parameters are established through beam flux and reflection high-energy electron diffraction measurements. InP and InGaP lattice matched to GaAs were grown and characterized by Hall measurements, photoluminescence, electroreflectance, x-ray diffraction, and transmission electron microscopy. The first microwave performance (f_t=44 GHz, f_{max}=65 GHz) of an InGaP/GaAs heterojunction bipolar transistor grown by solid-phosphorus source is reported. © *1995 American Vacuum Society.*

I. INTRODUCTION

The development of valved-phosphorus cracker has generated great interest in the field of III–V molecular-beam epitaxy (MBE). As MBE turns into a mature growth technology for As-containing compounds, it is desirable to incorporate a phosphorus source into the system for the growth of phosphides. This goal has been achieved by gas-source MBE (GSMBE) and chemical-beam epitaxy (CBE) in which highly toxic hydrides are used. However, the safety issues and gas-handling system involved for utilizing arsine and phosphine often make GSMBE and CBE much more complicated and costly compared to a solid-source MBE. The main problem of using solid phosphorus in an effusion cell is that when the P_4 molecules are condensed on cryopanels, white phosphorus is formed. White phosphorus is pyrophoric and has a very high vapor pressure, which may exceed the pumping capacity when the system warms up. This increases the fire hazard enormously.[1] There have been relatively few reports on phosphides grown by solid source MBE in the past.[2–4] Recently several groups have reported the growth of phosphides by a valved cracker. Wicks *et al.* first reported the growth of InGaP and InAlP by a valved cracker. High-quality InGaP and InGaAlP were grown by Mowbray *et al.*[6,7] and the band structure of InGaAlP was investigated. Reproducibility of the growth of InGaAsP/InP by two valved crackers was studied by Baillargeon *et al.*[8] These results are very encouraging since they demonstrate that it is possible to grow high-quality phosphides as well as arsenides in a MBE system without using hydrides.

In this article we report the first microwave performance of an InGaP/GaAs heterojunction bipolar transistor (HBT) grown by a solid source MBE using a valved-phosphorus cracker. Previous reports of InGaP/GaAs HBTs were mainly grown by GSMBE, CBE, or metalorganic chemical vapor deposition (MOCVD). The purpose of this work is to establish the growth parameters of the valved-phosphorus cracker and achieve device performance which is comparable to similar devices grown by the aforementioned growth techniques.

II. EXPERIMENTAL DETAILS

The growth was performed in a modified Varian GEN-II CBE system. All the gas sources and injectors were replaced with solid sources. A turbopump was used as the main pump during growth. A liquid nitrogen cold trap was installed between the turbopump and the mechanical pump to prevent phosphorus accumulation in the mechanical pump oil. Reflection high-energy electron-diffraction (RHEED) was used to calibrate the growth rate of various materials. An EPI valved-phosphorus cracker was installed with 850 grams of 7N-red phosphorus. The red phosphorus was sublimated at 400 °C and a small amount of white phosphorus condensed on the inner wall of the cracker. The whole cracker was then heated from outside to 70 °C and the white phosphorus was sublimated. A micrometer-controlled needle valve adjusted the phosphorus flux. The cracking temperature was chosen by observing the phosphorus beam equivalent pressure (BEP) in the 10^{-5} Torr range as a function of cracking temperature. The BEP stopped changing as the temperature reached 800 °C or higher. The typical phosphorus BEP for growing InP and InGaP was $8–20\times10^{-6}$ Torr. The surface V/III ratio, which is defined as the ratio of P-induced over In-induced RHEED oscillation rate,[9] ranged from 1.5 to 2. The background pressure during the growth was typically 5×10^{-7} and 2×10^{-8} Torr (inside and outside the cryopanel, respectively). The chamber pressure went up to about 2×10^{-6} Torr when the cryopanel warmed up.

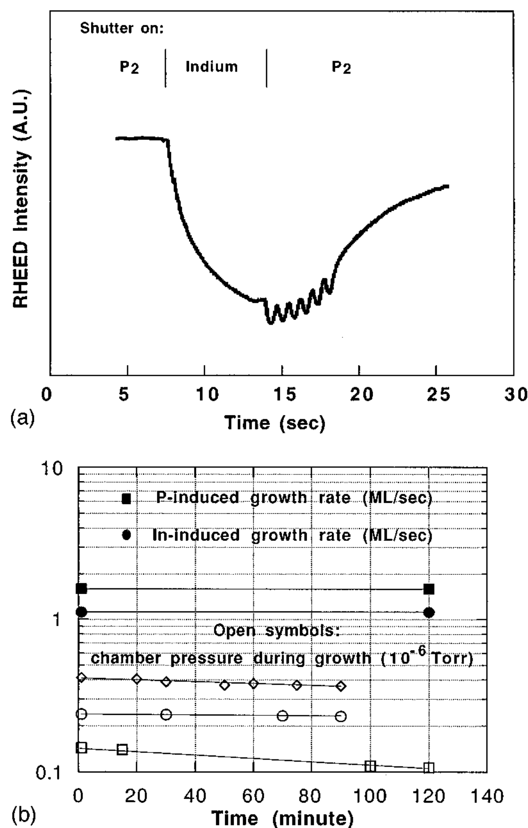

FIG. 1. (a) Phosphorus-induced RHEED oscillations observed on InP (001) surface. (b) The stability of P- and In-induced RHEED oscillation rate over a period of two hours. Open symbols are the chamber pressure recorded during three growths with different phosphorus flux.

III. RESULTS AND DISCUSSION

Although a highly stable phosphorus flux is not required while growing InP or InGaP, it is very important for mixed group-V materials, e.g., $In_xGa_{1-x}As_yP_{1-y}$, in which the composition is sensitive to the As/P ratio.[10] Preliminary study of the flux stability was performed by measuring phosphorus-induced RHEED oscillations [Fig. 1(a)] before and after a 2-h InP growth. As shown in Fig. 1(b), the phosphorus flux stays unchanged over two hours. The chamber pressure during growth tends to decrease over time, which is attributed to the variation of the ion gauge. The reproducibility of the cracker was also monitored by phosphorus-induced RHEED oscillations. Repeated RHEED oscillation measurements performed on the same InP substrate showed that the reproducibility of the phosphorus flux is comparable to that of the indium cell over several days.

Hall measurements performed on undoped InP layers showed that the cracking temperature affects the mobility and carrier concentration in undoped InP layers. 3-μm-thick InP layers grown at a substrate temperature of 480–500 °C with a cracking temperature of 1050 °C showed low room-temperature mobility ($\mu \approx 1000$ cm^2/V s), while carrier concentrations ranged from 2×10^{15} to 3×10^{16} cm^{-3}. This is probably caused by impurities coming from the shroud near the hot cracker. Similar phenomenon has been reported by Baillargeon *et al.*[11] and attributed to molecular impurities in the red phosphorus. This problem was not seen in samples grown with lower cracking temperature (850–900 °C). The Hall mobility and electron concentration at 300 and 77 K were 3200 cm^2/V s; 7.5×10^{15} cm^{-3} and 31 000 cm^2/V s; 3×10^{15} cm^{-3}, respectively. 10 K photoluminescence (PL) and electroreflectance (ER) were also measured (Fig. 2). The PL peak at 1.417 eV is assigned to D^0-X transition and the transition at 1.38 eV is attributed to D^0-A^0 transition.[12] The free exciton transition, which is not well resolved in the PL spectrum, is observed by ER as a sharp peak (FWHM=1.37 meV) at 1.4185 eV.

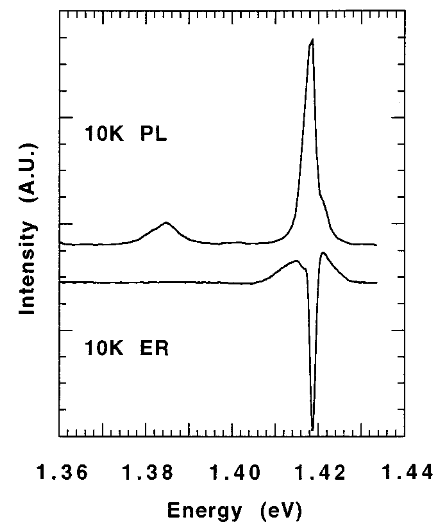

FIG. 2. 10 K PL and ER spectra of a 3-μm-thick undoped InP.

InGaP layers lattice-matched to GaAs was grown at 540 °C and characterized by x-ray rocking curve and transmission electron diffraction (TED). The x-ray FWHM of $In_{0.48}Ga_{0.52}P$ films is typically 10–20% larger than that of the GaAs substrate. TED patterns along both $[\bar{1}10]$ and $[110]$ zone axes were examined. The $[\bar{1}10]$ pattern only exhibit the Bragg reflections of the zinc blende structure. On the other hand, the $[110]$ pattern, as shown in Fig. 3, reveals two series of wavy streaks in the $1/2\ \overline{1/2}\ n$ equivalent position with a continuous value of n. These wavy streaks are due to a short-range ordered structure which has been observed in

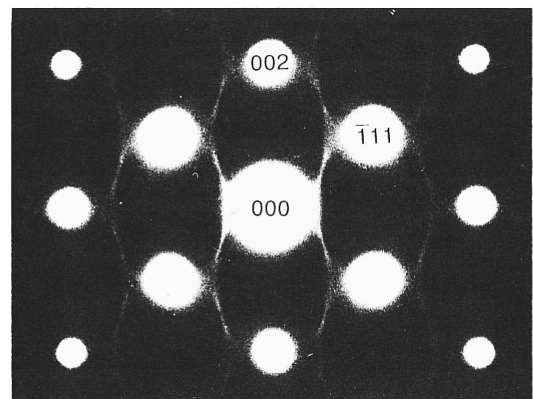

FIG. 3. $[110]$ zone axis transmission electron diffraction pattern of $In_{0.48}Ga_{0.52}P$ grown at 540 °C.

Layer	Thickness	Type	Doping
$In_xGa_{1-x}As$ x=0-0.3	150 Å	n+	1E19
GaAs	1000 Å	n+	1E19
InGaP	500 Å	n+	1E19
InGaP	1000 Å	n	5E17
GaAs	100 Å	p	5E18
GaAs	600 Å	p+	5E19
GaAs	5000 Å	n	2E16
GaAs	6000 Å	n+	1E19
GaAs	S.I. substrate		

FIG. 4. Structure of the InGaP/GaAs HBT.

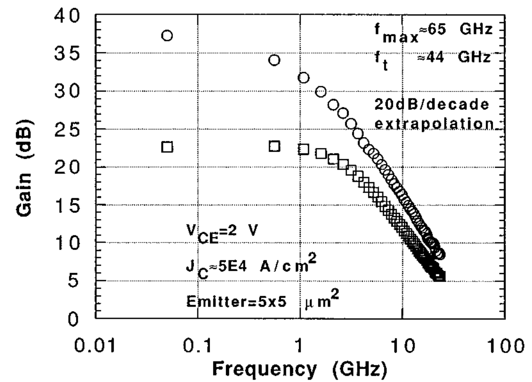

FIG. 6. Cutoff frequency (f_t) and maximum oscillation frequency (f_{max}) of a 5×5 μm device.

samples grown by MOCVD[13] at 550–600 °C and GSMBE at 500 °C.[14] As reported in the literature,[13,14] this short range order structure still have the bandgap of a normal crystal. The bandgap was about 1.9 eV as measured by PL at 300 K.

The small conduction band discontinuity between InGaP and GaAs and the large breakdown voltage of InGaP make InGaP/GaAs suitable for high speed or high power HBTs. The HBT structure is shown in Fig. 4. First, a Pd/Ge/Ti/Au metal system was used as the emitter contact, which then served as an etch mask for base recess. Then Pd/Zn/Pd/Au was deposited as the base contact. The separation between emitter and base contacts was about 0.2 μm. The base/collector mesa is achieved using a combination of reactive ion etching (RIE) and chemical etching to reduce undercut and damage. Collector contacts were made with the same metal system as the emitter contacts. Finally, a PECVD SiO_2 layer and a Ti/Al/Ti/Au layer were deposited as interconnect dielectrics and metals. After fabrication, devices were annealed under nitrogen atmosphere at 350 °C for 1 min using a hot plate. dc results were measured using a Hewlett-Packard HP4145B and high-frequency performance evaluated by a HP8510 system.

The dc current gain (β) of large area (40×40 μm^2) devices was 20. The ideality factors of the collector and base current were 1.02 and 1.41, respectively. The rather large base current ideality factor is possibly due to the recombination centers formed by the intermixing at the emitter-base heterojunction. Further optimization of the growth procedure at this junction is necessary. The common-emitter $I-V$ characteristic is shown in Fig. 5. Good breakdown voltage (BV_{ce0}≈17 V and BV_{cb0}≈24 V) are observed for the large-area device.

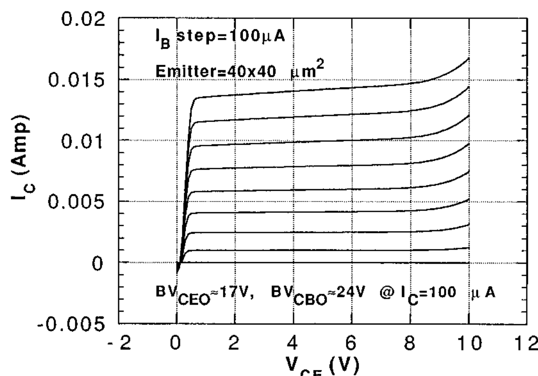

FIG. 5. Common-emitter $I-V$ characteristic of the HBT.

High-speed measurements were performed on a small-area (5×5 μm^2) device. The current-gain cutoff frequency (f_t) and the maximum frequency of oscillation (f_{max}) were estimated to be 44 and 65 GHz, respectively (Fig. 6). To our knowledge, this is the first microwave performance reported on an InGaP/GaAs HBT grown by a valved-phosphorus cracker.

IV. CONCLUSION

In conclusion, we demonstrated the valved cracker to be a viable phosphorus source in a solid-source MBE system. The operating parameters were established by both beam flux and RHEED measurements. InP and InGaP layers were grown by the cracker and characterized by Hall measurements, PL, ER, x-ray diffraction, and transmission electron microscopy. The first microwave performance of an InGaP/GaAs HBT grown by solid-source MBE was reported. Further investigation on the stability of wide-range flux control is necessary for the growth of mixed-group-V materials of any composition. Valved crackers offer a means of growing phosphides in a MBE with minimal system modification and no toxic gases. It should be noted that this technology is not limited to phosphorus. In principle, MBE of other high-vapor-pressure elements could also benefit from valved crackers.

ACKNOWLEDGMENT

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