

Wide-dynamic-range, fast-response CBr₄ doping system for molecular beam epitaxy

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(Received 7 October 2009; accepted 1 February 2010; published 29 March 2010)

The authors report the design and performance of a versatile carbon doping system for solid-source molecular beam epitaxy using carbon tetrabromide (CBr₄). This system is capable to achieve three orders of magnitude in doping by changing the CBr₄ temperature along with varying the CBr₄ leak rate into the growth chamber. The CBr₄ temperature is controlled using thermoelectric coolers and thus can be adjusted easily and quickly. The CBr₄ vapor pressure increases more than 1 decade when its temperature increases from -5 to 20 °C. The CBr₄ leak rate is controlled using six different diameter orifices connected in parallel, and the flow to each orifice can be switched on and off independently using a pneumatic valve. The fast response time of these pneumatic valves enables us to change the doping abruptly. This system is suitable for growing sophisticated structures, which require wide doping range and fast changes in doping. © 2010 American Vacuum Society.

[DOI: 10.1116/1.3357305]

I. INTRODUCTION

Compared to other *p*-type dopants in (Al)GaAs materials, such as beryllium and zinc, carbon has a very low diffusion coefficient¹ and is less dependent on the composition,² which make it attractive in the growths of some electronic and optoelectronic devices. Since the first successful report in 1993,³ carbon tetrabromide (CBr₄) has become widely used as a carbon source in conventional molecular beam epitaxy (MBE). This is because high doping efficiency and high-quality films can be achieved using CBr₄. Since no carrier gas is needed for transporting CBr₄ gas, a CBr₄ doping system can be easily incorporated into MBE without modifying the existing pumping system.

For most growths, currently available CBr₄ doping systems can usually meet their growth requirements. However, these systems are not ideal for growing complicated structures which require a wide doping range and fast doping change such as vertical-cavity surface-emitting lasers (VCSELs). In order to simultaneously minimize the optical losses and electrical resistance, the distributed Bragg reflectors (DBRs) in VCSELs have to be band gap engineered. This is especially important for the *p*-DBR due to higher free carrier absorption loss and lower mobility of holes. These band-gap-engineering schemes usually involve several doping levels in the range of 10¹⁷–10¹⁸ cm⁻³ within a DBR period, which is ~150 nm for 980 nm VCSELs.⁴ Therefore, the CBr₄ doping system must be capable of changing the

doping quickly to minimize the growth time. In addition, a high carrier concentration in the 10²⁰ cm⁻³ is desirable for the *p*-contact layer to reduce the contact resistance. This means that the CBr₄ doping system must be operated over three orders of magnitude in doping for a single growth.

In this article, we report the design and performance of a versatile CBr₄ doping system for MBE, which addresses the requirements of wide doping range and fast doping change. Wide dynamic range is realized by changing the CBr₄ vapor pressure through a closed-loop temperature control as well as changing the CBr₄ leak rate into the growth chamber. The CBr₄ leak rate is controlled digitally by switching on and off six pneumatic valves and thus can be varied quickly.

II. SYSTEM DESIGN

Most of the CBr₄ doping systems for MBE operate similarly in principle by performing at least two main functions. One is to regulate the CBr₄ base vapor pressure, which is typically in the tens and hundreds of millitorr during operation. The other is to reduce the amount of CBr₄ injecting into the growth chamber using constrictions such as (variable) leak valves or orifices. This is necessary because the CBr₄ beam equivalent pressure less than 10⁻⁶ Torr is usually sufficient for most growths. Different systems use different approaches to achieve these two functions. For example, the CBr₄ base vapor pressure can be regulated directly using closed-loop pressure control or indirectly using closed-loop temperature control. The doping concentration can be ad-

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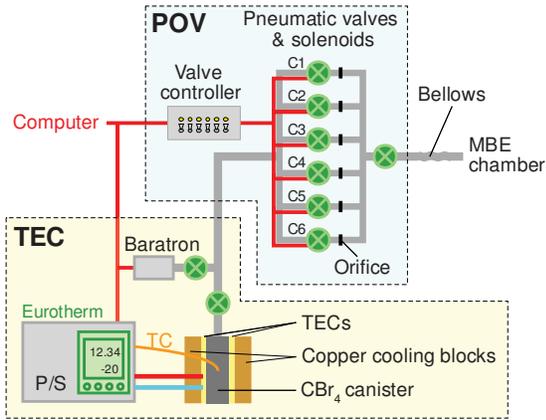


FIG. 1. (Color online) Schematic of the CBr₄ doping system.

justed by changing the CBr₄ vapor pressure or varying the leak rate, i.e., the conductance of the constrictions.

Figure 1 shows the schematic of our CBr₄ doping system, which is divided into the thermoelectric cooler (TEC) system and the parallel orifice valve (POV) system according to their functions. The TEC system is used to control the CBr₄ base vapor pressure and the POV system is used to variably reduce the amount of CBr₄ injecting to the growth chamber. In the following, we will describe these two systems in details.

A. Thermoelectric cooler system

Basically, the TEC system is a temperature-controlled CBr₄ container with the accessory electronics and plumbing as illustrated in the lower box in Fig. 1. Instead of using a water bath, the temperature of the container is controlled using TECs.⁵ The core of this system is a custom-designed module shown in Fig. 2. A valved stainless steel canister, which is $25 \times 25 \times 50$ mm³ in size, contains solid CBr₄ crystals. The canister is fairly small so that its temperature can be changed quickly. Two 25×25 mm² TECs are sandwiched between one side of the canister and a copper block which has cooling water running through to maintain it roughly at room temperature. There is a total of four TECs for two sides of the canister. These TECs, which have a V_{\max} of 3.6 V and an I_{\max} of 14.7 A at 27 °C, are electrically connected in series to have a manageable operating current. The module is wrapped with thermally insulating foam to reduce heat exchange from the environment. In addition, the whole module is enclosed in a sealed acrylic box. When the CBr₄ canister is operated below the dew point, the box has to be purged with dry nitrogen to prevent water condensation, which can thermally shorten the cold and hot sides of the TECs and significantly reduce the cooling power.

The temperature of the canister is monitored using a type-K thermocouple, which is spot welded on the canister and feeds into a Veeco dc power supply with a Eurotherm temperature controller. It should be noted that there are temperature gradients from the sides that the TECs touch and the monitored spot due to nonuniform cooling. In the following,

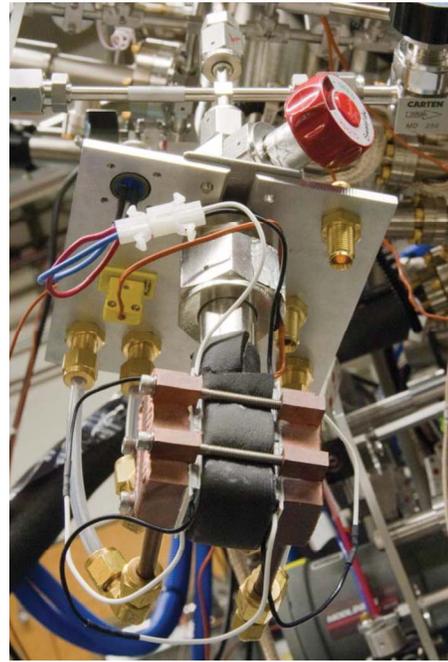


FIG. 2. (Color online) Photograph of the TEC module.

the “CBr₄ temperature” is referred to the temperature at the monitored spot unless otherwise specified. With a closed-loop control, the CBr₄ temperature can be accurately maintained within ± 0.2 °C of the set point.

One of the advantages of using TECs is that heat transfer is bidirectional, which means that the TECs can either cool down or heat up the CBr₄ canister actively by reversing the direction of the current flow. However, because the power supply currently being used is unipolar, the TECs can only cool down the canister, which leads to a slower response time when warming up the canister as will be shown later.

A capacitance manometer, Baratron, was installed to monitor the CBr₄ vapor pressure when the system is in use. However, it was soon discovered that the Baratron constantly outgases hydrogen. Without any pumping, the hydrogen vapor pressure, which increases with time, contributes to the total vapor pressure read by the Baratron. Therefore, an UHV manual valve was installed to prevent hydrogen from entering the gas manifold during growth.

B. Parallel orifice valve system

Figure 3 shows a photograph of the POV system. To avoid potential inconsistency with variable leak valves at small openings, our system uses fixed orifices to achieve small conductance. As shown in the schematic in Fig. 1, the gas line from the TEC system is first split into six lines and each line has a pneumatic valve followed by an orifice with different diameters. After the orifices, these six gas lines merge together and then connect to the gas inlet on the source port through a flexible bellows. Since these air-operated pneumatic valves have a switching time in the order of hundreds of milliseconds, fast doping switching is possible.

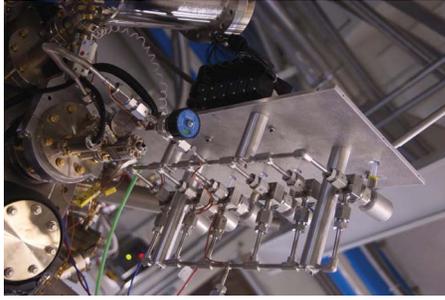


FIG. 3. (Color online) Photograph of the POV system.

The idea of the POV system is quite straightforward. If these six orifices ideally have conductance of 1/2/4/8/16/32 at the given CBr₄ vapor pressure, then a total of 2⁶=64 doping levels can be achieved by permutation, provided the doping does add up. Currently, the nominal diameters of the orifices associated with pneumatic valves C1, C2, C3, C4, C5, and C6 are 250, 200, 150, 100, 75, and 50 μm , respectively. To prevent CBr₄ from condensing on the tubing, all the lines are constantly baked between 60 and 70 $^{\circ}\text{C}$. This temperature should be low enough to avoid thermally cracking CBr₄, which should happen on the substrate.

In our system, pumps can be eliminated except through the growth chamber. This makes the system compact and also reduces the wasted source materials. This is possible because the CBr₄ vapor pressure is controlled by its temperature and can be reduced without pumping. Also, the CBr₄ flow can be completely turned off and thus does not need a pump when not in use.

III. RESULTS AND DISCUSSION

The CBr₄ doping system was characterized on a Veeco Gen III solid-source MBE system. All the calibration samples were grown at 580 $^{\circ}\text{C}$ and a growth rate of $\sim 1 \mu\text{m/h}$ with a V/III ratio of ~ 30 on semi-insulating GaAs (100) substrates.

A. Thermoelectric cooler system results

For the TEC system, it is desirable that at a given CBr₄ temperature, the CBr₄ vapor pressure is stable, reproducible, and independent of the amount of CBr₄ being depleted into the growth chamber. In addition, the transient time for changing the CBr₄ vapor pressure is ideally to be short.

To evaluate the stability and transient response of the TEC system, the following experiment was performed. The CBr₄ was cooled down from room temperature to -5°C half an hour earlier. At $t=0$, valve C5 was opened so that most of the undesired hydrogen from the Baratron can escape into the growth chamber. After 1 h, the temperature was raised to 20 $^{\circ}\text{C}$, and finally, the temperature was lowered back to -5°C after another 1 h. The CBr₄ temperature and vapor pressure were recorded every 10 s over the course of 3 h. The result is plotted in Fig. 4. The initial drop in the vapor pressure is due to the accumulated hydrogen being pumped out when the valve was first opened.

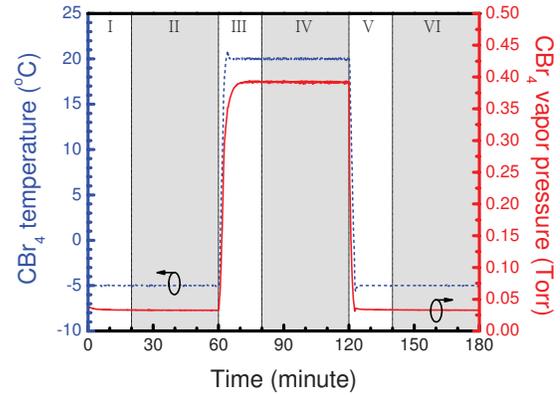


FIG. 4. (Color online) CBr₄ temperature and vapor pressure measured for 3 h. At $t=60$ m and $t=120$ m, the temperature set point was changed from -5 to 20 $^{\circ}\text{C}$ and back to -5°C , respectively.

The CBr₄ temperatures averaged over 40 m in regions II, IV, and VI are the same as the set points and the temperature variations are within $\pm 0.2^{\circ}\text{C}$. The averaged CBr₄ vapor pressures in regions II, IV, and VI are 0.0328, 0.3920, and 0.0330 Torr, respectively. The vapor pressure increases more than ten times when the temperature increases from -5 to 20 $^{\circ}\text{C}$. In addition, the vapor pressure variations are within $\pm 2.5\%$ of their averaged values, which indicates that the system is quite stable.

To see how consistent this system is, the same experiment was repeated five times at different times. Table I summarizes the averaged CBr₄ vapor pressure for three different regions over five runs. It is evident that the vapor pressure is indeed consistent at the same temperature. Although the vapor pressure in region VI is always slightly higher than that in region II, the difference is quite small and within 1%.

For a given CBr₄ temperature, its vapor pressure should ideally be maintained constant and is independent of the amount of CBr₄ being depleted into the growth chamber. Since the CBr₄ base vapor pressure is several orders of magnitude higher than the pressure after the orifices, this should be the case. To verify it, the vapor pressure at a CBr₄ temperature of -5°C was recorded while different combinations of valves were being opened. The result is shown in Fig. 5. The difference between the worse case, i.e., all valves

TABLE I. Summary of the averaged CBr₄ vapor pressure in three 40 m periods at different CBr₄ temperatures repeated for five times.

	CBr ₄ vapor pressure averaged over the region (Torr)		
	Region II (20–60 m)	Region IV (80–120 m)	Region VI (140–180 m)
Run 1	0.0329	0.3920	0.0331
Run 2	0.0329	0.3916	0.0331
Run 3	0.0327	0.3914	0.0330
Run 4	0.0326	0.3917	0.0329
Run 5	0.0328	0.3920	0.0330
Five runs averaged	0.0328	0.3917	0.0330

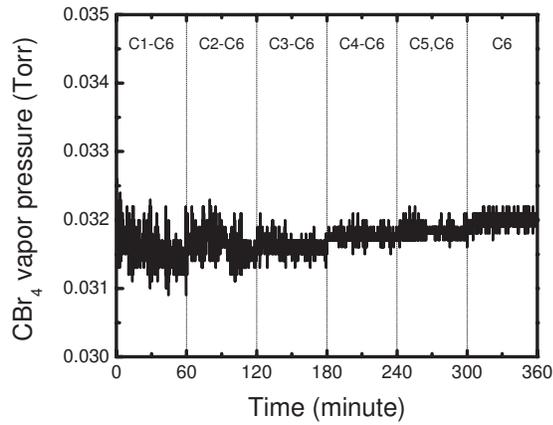


FIG. 5. CBr₄ vapor pressure with different valves being opened at a CBr₄ temperature of -5°C . The valves that were opened for each period are labeled.

were opened (first region), and the best case, i.e., only the smallest valve was opened (last region), is indeed fairly small. The vapor pressure is slightly smaller than the previous value, possibly due to a lower partial pressure of hydrogen because all the valves were opened at the beginning.

To evaluate how fast the system responds to a change in the temperature set point, we analyzed the transient in regions III and V in Fig. 4. The rise time (10%–90%) and fall time (90%–10%) for the temperature changing between -5 and 20°C are approximately 2 and 1.5 m, respectively. It should be noted that the temperature controller was optimized to provide better stability at the expense of a slower response. The rise and fall times for the vapor pressure are approximately 4 and 2 m, respectively. The reason for a slower rise time can be explained as follows. Since the equilibrium vapor pressure is determined by the lowest temperature in the canister, we need to consider how the coldest spot reaches its steady-state temperature. For active cooling, the coldest spot in the canister should be where it touches the TECs and thus, the vapor pressure drops faster. A close look at the figure reveals that the measured CBr₄ vapor pressure actually dropped faster than the vapor pressure estimated from the steady-state CBr₄ temperature (the relation between the vapor pressure and temperature will be discussed shortly). On the other hand, when the temperature set point is higher than the CBr₄ temperature, no power is provided to the TECs and the canister warms up passively. Because the heat needed to warm up the canister is transferred from the environment, the coldest spot is where the heat transfer is the least efficient and is likely not the monitored spot. When the CBr₄ temperature overshoots, the TECs start to cool down while the coldest spot has yet reached its steady-state temperature. Therefore, it takes longer time to settle due to the undesired cooling. This is why the rate of the vapor pressure increasing slowed down right after the overshoot. This spatially nonuniformity in cooling and warming up results in the asymmetry in the rise and fall times. Active heating using the TECs should improve the rise time and can be done with a bipolar power supply.

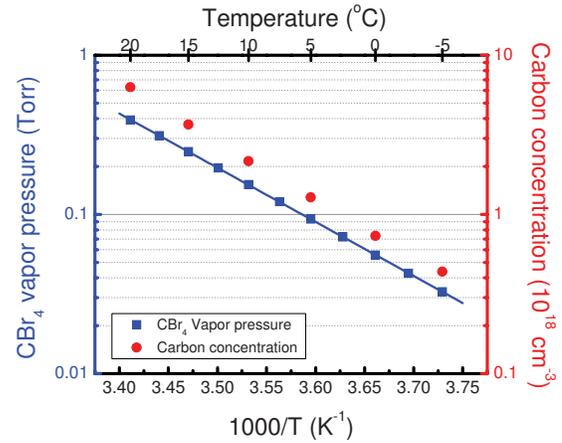


FIG. 6. (Color online) CBr₄ vapor pressure and carbon concentration measured by SIMS as a function of the CBr₄ temperature.

The relationship between the CBr₄ temperature and its vapor pressure is also of interest. The vapor pressure at temperatures between -5 and 20°C in a 2.5°C step was measured, and the result is plotted (squares) in Fig. 6. The data can be well fitted by the following equation:

$$\log_{10}(P) = 11.189 - 3398.96/T,$$

where P is the vapor pressure in Torr and T is the temperature in Kelvin. The vapor pressure at a given CBr₄ temperature is lower than what has been reported previously.³ This can partially result from the temperature difference at the monitored and the coldest spots.

B. Parallel orifice valve system results

The POV system controls the CBr₄ leak rate into the growth chamber at a given CBr₄ vapor pressure. To predict the amount of CBr₄ leaking into the chamber, it is helpful to know the gas flow regime for the CBr₄ molecules under the operating conditions. Its mean free path is estimated to be in the order of hundreds of micron, which is close to the diameter of the orifices. Therefore, this system is operated in either the molecular flow regime or the transition flow regime, depending on the orifice sizes and vapor pressure.⁶ When in the molecular flow regime, gas-wall collisions dominate. The conductance simply depends on the size of the orifices and is independent of the vapor pressure. On the other hand, the conductance in the transition flow regime also depends on the vapor pressure, and higher vapor pressure gives higher conductance.

To see how the carbon concentration varies with the CBr₄ vapor pressure, a secondary ion mass spectroscopy (SIMS) calibration sample was grown. The sample has six 200 nm GaAs:C layers grown at different CBr₄ temperatures, from 20 to -5°C in a 5°C step, and one 20 nm undoped GaAs layers after each GaAs:C layer. The valve that opened during the growth is C5. The SIMS result is plotted in Fig. 7. The carbon spikes at the surface and the epi-substrate interface are due to carbon contaminations from the environment. In each plateau, the concentration is fairly flat, which means

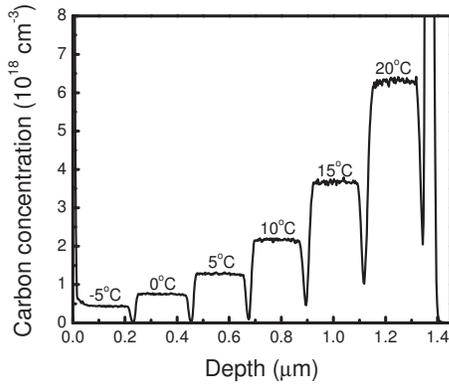


FIG. 7. SIMS profile for a structure with six GaAs:C layers grown at different CBr₄ temperatures. Only valve C5 was switched on and off during the growth. The CBr₄ temperature for each layer is labeled on the top of each plateau.

this system is quite stable. The averaged carbon concentration for each plateau is also shown as circles in Fig. 6. As the temperature increases, the carbon concentration increases faster than predicted from the vapor pressure assuming constant conductance. This can be seen in Fig. 6 that the distance between the square and circle increases at higher CBr₄ temperatures. This is because the mean free path is reduced at higher temperatures, and gas-gas collisions start to play a role in the gas flow, i.e., deviating from the molecular flow regime. The deviation should be more profound with larger orifices and higher vapor pressure.

Another SIMS calibration sample to determine the carbon concentration for different valve openings at a CBr₄ temperature of -5°C was also grown. The result is shown in Fig. 8. The valves that were opened during each plateau are labeled on the top. The averaged carbon concentration for all the valve combinations in the sample is listed in Table II. Clearly, the CBr₄ flux from the individual valve does add up as expected since the total conductance should be the sum of the individual conductance when connected in parallel.

To see how consistent the doping concentration is, three $1\text{-}\mu\text{m}$ -thick GaAs:C calibration samples were grown on different days. The CBr₄ temperature was maintained at -5°C

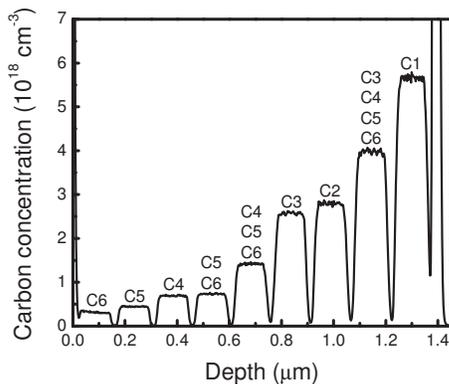


FIG. 8. SIMS profile for a structure with nine GaAs:C layers with different valves being opened. The CBr₄ temperature was kept at -5°C . The shutters that were opened for each layer are labeled on the top of each plateau.

TABLE II. Carbon concentration for different valve openings at a CBr₄ temperature of -5°C measured by SIMS.

Valves opened	Concentration (10^{18} cm^{-3})	Sum of individual valves (10^{18} cm^{-3})
C6	0.3	0.3
C5	0.42	0.42
C4	0.69	0.69
C5, C6	0.73	0.72
C4, C5, C6	1.42	1.41
C3	2.56	2.56
C2	2.80	2.80
C3, C4, C5, C6	3.98	3.97
C1	5.66	5.66

and valve C3 was open. The carrier densities at room temperature measured by Hall are 2.41×10^{18} , 2.41×10^{18} , and $2.47 \times 10^{18}\text{ cm}^{-3}$. These values are indeed reasonably close. According to the SIMS result, the carbon concentration at the same growth condition is $2.56 \times 10^{18}\text{ cm}^{-3}$, which means the electrical activation is around 95%, close to what was reported by other groups.³

Two more samples were grown to make sure three orders of magnitude in doping can be achieved. One was grown at a CBr₄ temperature of -5°C with C6 open and the other was grown at a CBr₄ temperature of 10°C with all the valves open. The carrier densities, measured by Hall, are 2.73×10^{17} and $1.14 \times 10^{20}\text{ cm}^{-3}$, respectively. Almost three orders of magnitude in doping have been achieved. Lower carrier density should be possible with lower CBr₄ temperatures.

IV. CONCLUSION

A versatile CBr₄ doping system for MBE was designed, built, and characterized. By using thermoelectric coolers to control the CBr₄ temperature, accurate and stable CBr₄ vapor pressure can be achieved reproducibly. Furthermore, the vapor pressure can be changed over ten times in only 4 m. Fast switching doping is realized by independently turning on and off the flow to six orifices with different diameters using pneumatic valves. The capability to change both the CBr₄ vapor pressure and conductance to the chamber enables us to achieve three orders of magnitude in the doping concentration, making this CBr₄ doping system suitable for growing structures with sophisticated doping profiles and wide doping range.

ACKNOWLEDGMENTS

The authors would like to thank the supports and valuable discussions with the people in the MBE laboratory at the University of California, Santa Barbara.

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