REVIEW

How Gallium Arsenide Wafers are Made

Minoru Kitsunai* and Takayoshi Yuki†
* Tsukuba Plant, Mitsubishi Kasei Corp., 1000 Higashi Mamiana, Ushiku City, Ibaraki 300-12, Japan, and † Division of Electronics Materials and Instruments, Mitsubishi Kasei Corp., 2-5-2 Marunouchi, Chiyoda-ku, Tokyo 100, Japan

Ten Japanese gallium arsenide wafer manufacturers voluntarily formed The Japan Manufacturers' Society of Compound Semiconductor Materials (JAMS-CS) in 1983. This report summarizes the theories, the systems, and the operations of gallium arsenide production: the gradient freeze (GF) method, the liquid-encapsulated Czochralski (LEC) method, the wafer processing, the vapor-phase epitaxial (VPE) growth method, the liquid-phase epitaxial (LPE) growth method, the metalorganic chemical vapor deposition (MO-CVD) method and the molecular beam epitaxial (MBE) method.

Keywords: Gallium arsenide, production, safety methods

1 INTRODUCTION

Gallium arsenide (GaAs) wafers are used as substrates for many kinds of electronic devices, for example light emitting diodes, field-effect transistors and laser diodes, because GaAs has light-emitting properties, high electron mobility, and other useful properties. GaAs is the key material for the super-high-speed computer, so many manufacturers are competing vigorously in research and development. Therefore, the most sophisticated and improved systems are secret. There has been little information about recent systems, operations, and working conditions of actual GaAs plants. In a previous study,[1] the GaAs process for photovoltaic cells was considered hazardous. In a recent study,[2] workers exposed to GaAs were able to stay relatively healthy in the clean room of the GaAs plant, in which the atmospheric arsenic concentration was kept under 0.02 mg m^{-3}. As the LD_{50} value of GaAs is 4700 mg kg^{-1}, it is necessary to pay attention to the health of workers.[3] The production processes of GaAs should be revealed as fully as possible, but of course this knowledge is very important and valuable for the GaAs manufacturers. Therefore, this report can review only the basic theories, systems and operations of the manufacturing methods which are adopted by one member of the JAMS-CS. The aim of this report is to bring about a better understanding of recent production methods for GaAs wafers.

2 JAMS-CS

Table 1 shows the organization of The Japan Manufacturers' Society of Compound Semiconductor Materials (JAMS-CS). JAMS-CS aims at promotion of the III–V compound semiconductor business by collection of information, and was formed in 1983.

3 APPLICATIONS OF GaAs WAFERS

Table 2 shows usage of GaAs wafers. GaAs has light-emitting properties. Thus, visible-light-emitting diodes (LED) are used as display lamps for home electric goods, outdoor displays facsimile machines and printers. Infrared LEDs are used in remote controllers, autofocus cameras and photocouplers. Laser diodes are used as the light sources for optical communication, optical disks and laser printers. As the electron mobility in GaAs is about five times higher than that in silicon, GaAs wafers are used as integrated circuits (IC) substrates for super-high-speed computers. Field-effect transistors (FETs) are highly responsive. Therefore, FETs are used as very-low-noise amplifiers for the microwave systems, portable telephones and direct broadcasting systems by satellite. GaAs has electromagnetic properties, so Hall sensors are used as rotor meters and motor-positioning sensors. As

CCC 0268–2605/94/030167–08

Received 10 December 1993
Accepted 7 January 1994

Table 1 JAMS-CS membership and products

	Products								
	GaAs					GaP			InP
Member	BG[a]	LEC[b]	EPI[c]	FET[d]	Chip	LEC[b]	EPI[c]	Chip	LEC[b]
Dowa Mining Co. Ltd	O	O	O		O				O
Furukawa Electric Co. Ltd		O	O	O					O
Hitachi Cable Ltd	O	O	O	O	O				O
Mitsubishi Kasei Corp	O	O	O	O	O	O	O	O	
Mitsubishi Material Corp.	O	O		O					O
Japan Energy Corp.		O		O					O
Shin-Etsu Handoutai Co. Ltd		O	O		O	O	O	O	O
Showa Denko K.K.	O	O	O	O	O	O	O	O	O
Sumitomo Electric Ind. Ltd	O	O	O	O	O				O
Sumitomo Metal Mining Co. ltd		O				O			O

O, Product is manufactured by the company indicated.
[a] GaAs mirror wafer made by boat-grown (BG) method (GF method or HB method).
[b] Mirror wafer made by liquid-encapsulated Czochralski method.
[c] Epitaxial wafer made by VPE, LPE, MO-CVD or MBE method.
[d] Epitaxial wafer made by VPE method for field-effect transistors.

GaAs is thermally stable and has photoelectric properties, GaAs solar cells are used as long-lived and high-efficiency generators for satellites.

3.1 Production of GaAs ingots[4]

Figure 1 shows the production volumes of GaAs ingots in Japan. This volume is based on the value estimated by Furukawa Co. Ltd of the shipping volume of high-purity metallic arsenic. GaAs production volume increased rapidly in 1986, and, has levelled off recently, since the estimated volume of integrated circuit (IC) demand had been too great.

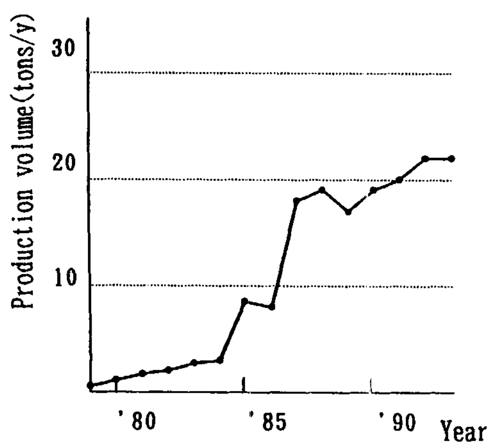

Figure 1 Production of GaAs ingots in Japan.

3.2 Production of arsenic[4]

Figure 2 shows the world production and usage volumes of arsenic in 1990, when the world production volume as metallic arsenic was 36 200 tons of which 60% was consumed as wood preservatives, agricultural chemicals, etc., in the USA. Only a small amount of arsenic was used for the GaAs industry in Japan.

Table 2 Applications of GaAs

Property	Device	Uses
Light emission	Visible LED	Display lamp, outdoor display, facsimile machine, printer
	Infrared LED	Remote controller, autofocus camera, photocoupler
	Laser diode	Optical disk and fiber lamp, laser printer, positioning sensor
High-speed mobility	Integrated circuit	Super-high-speed computer
High frequency	Field-effect transistor	Microwave amplifier, portable telephone, direct broadcasting by satellite
Electromagnetism	Hall sensor	Rotor meter, motor-positioning sensor
Photoelectric activity	Solar cell	Satellite generator

4 THE MANUFACTURING PROCESS

Table 3 shows the manufacturing process, from ore to electric goods. GaAs wafer manufacturers and some electric companies produce GaAs epitaxial-growth wafers (Epi wafer) and LED chips.

Table 4 shows the processes and systems from high-purity (99.9999%) gallium and arsenic to GaAs mirror wafers (GaAs wafer) and Epi wafers for some kinds of devices. The gradient freeze (GF) method, the vapor-phase epitaxial (VPE) growth method and the liquid-phase epitaxial (LPE) growth methods are widely used and traditional. The liquid-encapsulated Czochralski (LEC) method is comparatively new. Some mirror wafers are sold, and the others are used as epitaxial growth substrates. Metalorganic chemical vapor deposition (MO-CVD) and the molecular beam epitaxial (MBE) method have been developed and put to practical use recently.

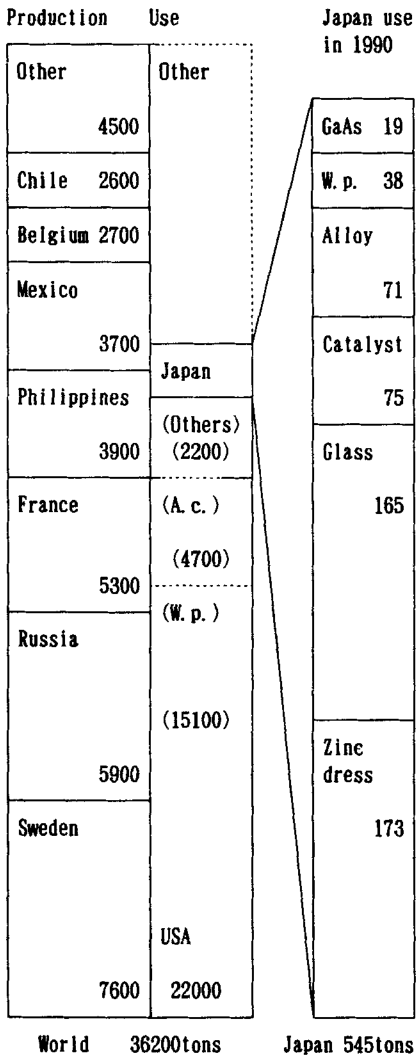

Figure 2 Production of arsenic in 1990. A.c., agricultural chemicals; W.p., wood preservatives; data in parentheses are a breakdown of the total USA.

4.1 GF method[5]

Figure 3 shows the GF method. The ingot is crystallized horizontally in the quartz boat, with a very gradually changing of temperature gradient. Gallium is kept in the locker in a bottle. Gallium and arsenic are weighed and charged into the quartz boat on the clean bench. After degassing, the vessel is set in the GF furnace. When the temperature rises over 600 °C, arsenic volatilizes, and reacts with the gallium. GaAs is produced and dissolves in the gallium solution first, and all of the gallium is changed eventually to GaAs, which melts at 1238 °C. Next, the furnace is inclined to contact the seed with the melt, and fixed. As the temperature gradient falls very slowly by automatic control, GaAs single-crystal ingots are produced. After cooling, the quartz boats are cut in a glove box in order to remove the GaAs single-crystal ingots. The GF method produces low-defect and high-quality crystals, but cannot produce crystals bigger than 3 in (~7.5 cm) diameter. The horizontal Bridgman (HB) method is adopted by some manufacturers.[6]

4.2 LEC system[7]

Figure 4 shows the LEC system. After the rotating seed is dipped at the surface of the GaAs melt, the seed is pulled up very slowly. The cylindrical single crystal is grown automatically by computer control. The advantage of the LEC method are low loss in wafer processing, and flexibility for mass production, because a large amount of GaAs is able to be charged and crystallized comparatively speedily.

4.3. Wafer processing

Figure 5 shows the wafer processing flow. This process consists of slicing, edging, lapping, mounting and polishing steps. Some steps include washing and drying. The axis of the GaAs ingot is fixed, and the ingot is moved horizontally at very slow speed. The blade of an inner-diameter saw

Table 3 Processes from ore to electric goods

Process	Raw material and products	Manufacturer
	Ore	
Refining Metallization	↓	Mining company Chemical company
	High-purity GaAs	
Crystal growth Wafer processing Epitaxial growth	↓	GaAs wafer manufacturer Electronic company
	GaAs wafer Epi wafer LED chips	
Manufacture of devices	↓	Electronic company
	LED, LD, IC, FET	
Fabrication	↓	Electric company
	TV set, printer, display, computer, telephone, etc.	

with small fragments of diamond adhering to it rotates at high speed. A large amount of coolant is sprayed during slicing to keep this process wet and dust-free. In addition, the slicing machines are covered with ventilation hoods and operate automatically after GaAs ingots have been set. The edging machine has a grinding wheel with a hollow at which the edge of the wafer is ground, and is rounded to prevent cracking. The edging is also wet, covered, and operated automatically. Sliced wafers are lapped to smooth surfaces. The

Table 4 Processes and systems for GaAs wafers

Process	Raw material and product	System
	High-purity Ga and As	
Crystal growth	↓	GF furnace LEC puller
	GaAs ingot	
Slicing Polishing	↓	Slicing machine Polishing machine
	GaAs mirror wafer	
Epitaxial growth	↓	VPE furnace LPE furnace MO-CVD system MBE system
	VPE Epi wafer LPE Epi wafer MO-CVD Epi wafer MBE Epi wafer	

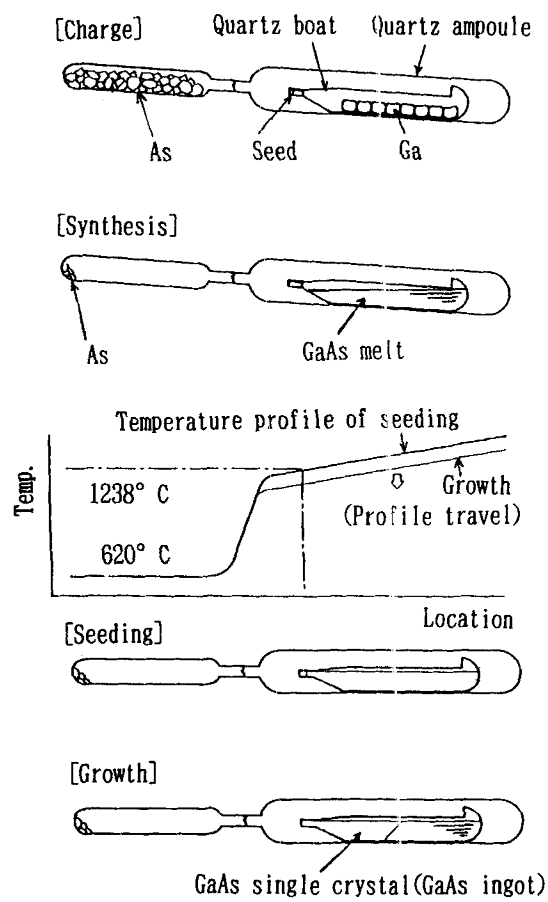

Figure 3 GF method: the steps are indicated in square brackets.

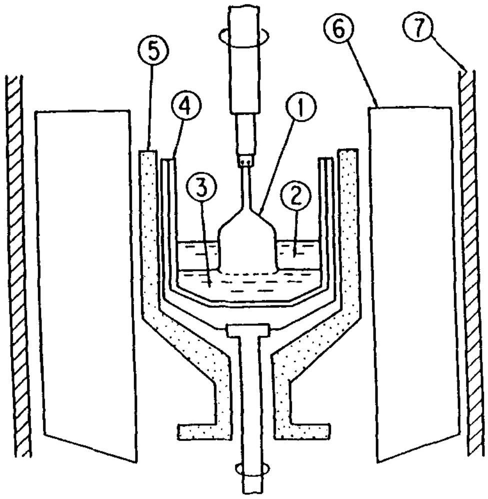

Figure 4 LEC system.

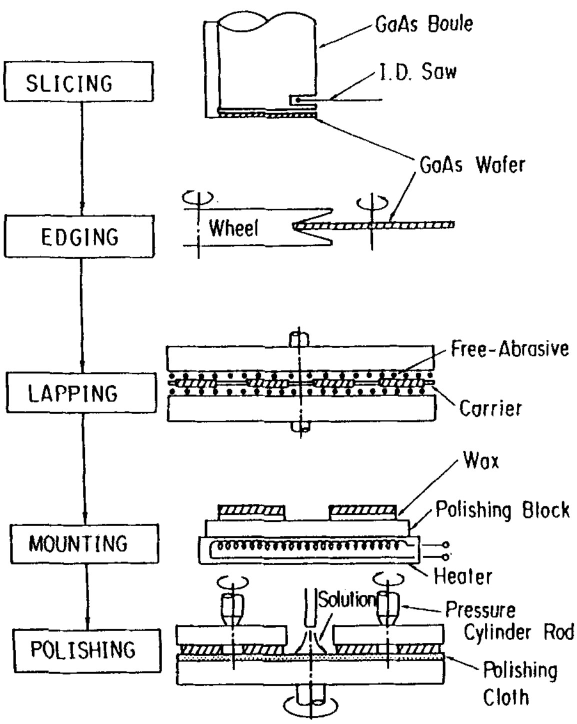

Figure 5 Wafer processing flow diagram.

lapping process is also wet with an abrasive slurry, and dust-free. When the polishing machine produces a GaAs mirror wafer in the high-grade clean room, the polishing process is also wet and dust-free.

4.4 VPE method

Figure 6 shows the structure of vapor-phase epitaxial growth wafers (VPE Epi wafers). The VPE method is able to produce thick and high-purity epitaxial layers. The improved VPE system innovated in 1969 is shown in Fig. 7. By this method, VPE Epi wafers for high-brightness LEDs have been made industrially at moderate cost. Using the much improved VPE system, VPE Epi wafers are produced. Mirror wafers are set on the holder, carried to the electric furnace and charged. After the door of the VPE hood has been closed, the worker inputs the program data for gas flow rate and heating, etc., from a local

GaAsP	20 μm	Active layer
GaAsP	20 μm	Graded layer
GaAs	300 μm	Substrate

(a)

GaAsP:N	20 μm	Active layer
GaAsP	20 μm	Constant layer
GaAsP	20 μm	Graded layer
GaP	300 μm	Substrate

(b)

Figure 6 Structure of VPE Epi wafers: (a) GaAsP/GaAs; (b) GaAsP/GaP.

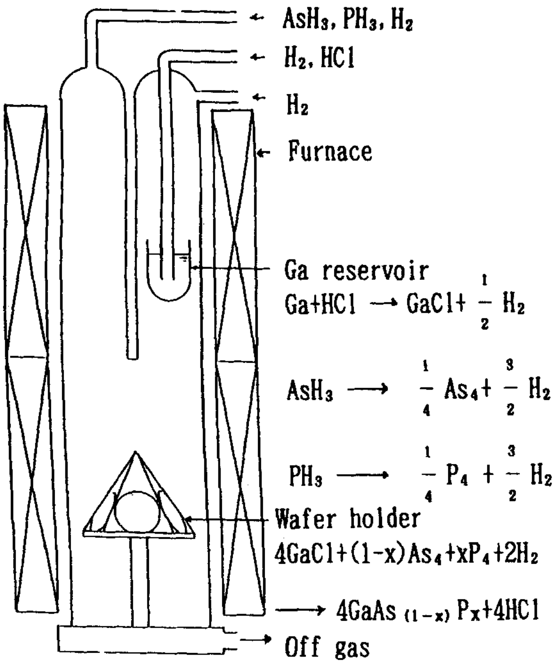

Figure 7 VPE system.

computer in the control room. VPE growth is operated automatically. When epitaxial growth is finished, the furnace is cooled down. VPE Epi wafers are taken out, after the quartz tube has been filled with nitrogen gas. Each VPE system has powerful ventilation. A large number of gas-leakage detectors are set in many places. Some exhaust gas treatment systems are installed. It is ensured that the flow of hazardous gas is stopped, while the workers are setting up the system, charging, and taking out wafers. VPE Epi wafers are made in a middle-grade clean room.

4.5 LPE method[9]

Slightly more complex structures with layers 60 μm thick made by the LPE method are shown in Fig. 8. GaAs or GaAlAs single-crystal layers are made on GaAs substrates by cooling GaAs or GaAlAs solutions. GaAs substrates are set in the hollows of a carbon boat, and the sliding boat assembly is placed in the LPE furnace, which is heated automatically at a fixed temperature until GaAs or GAAlAs is dissolved in the gallium solution. The boat is positioned over the GaAs substrates by moving a slider automatically, using a sliding-rod system. The GaAs single-crystal layers are grown by cooling the LPE furnace gradually. After a suitable time period, the solution on the LPE Epi wafer is removed by moving the slide again. After cooling the LPE furnace and replacing the atmosphere in it with nitrogen gas, the LPE Epi wafers are taken out on the clean bench. The workers keep watch on the control panel in the control room at all times except for charging, setting, and taking out substrates. Each LPE system has forced ventilation and a large number of gas leakage detectors are also set in many places. LPE Epi wafers are also made in a middle-grade clean room.

4.6 MO-CVD method[10]

Figure 9 shows the structure of MO-CVD and MBE Epi wafers. The major part of these wafers are GaAs substrates, because many epitaxial growth layers are very thin. More complex densely packed, and thinner layers have been produced by these methods recently. A layer 0.01 μm thick can be grown by the MO-CVD method. Moreover, a layer 0.002 μm thick, which is of a molecular size, is able to be grown by the MBE

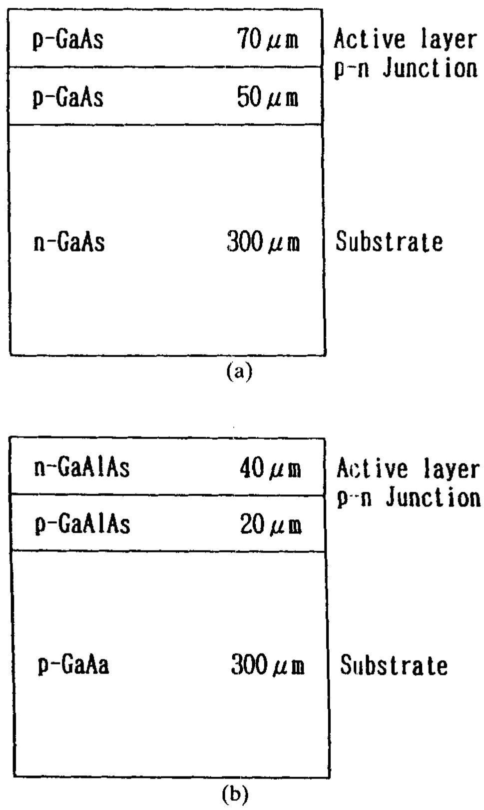

Figure 8 Structure of LPE Epi wafers: (a) standard infrared Epi wafer; (b) high-brightness red Epi wafer.

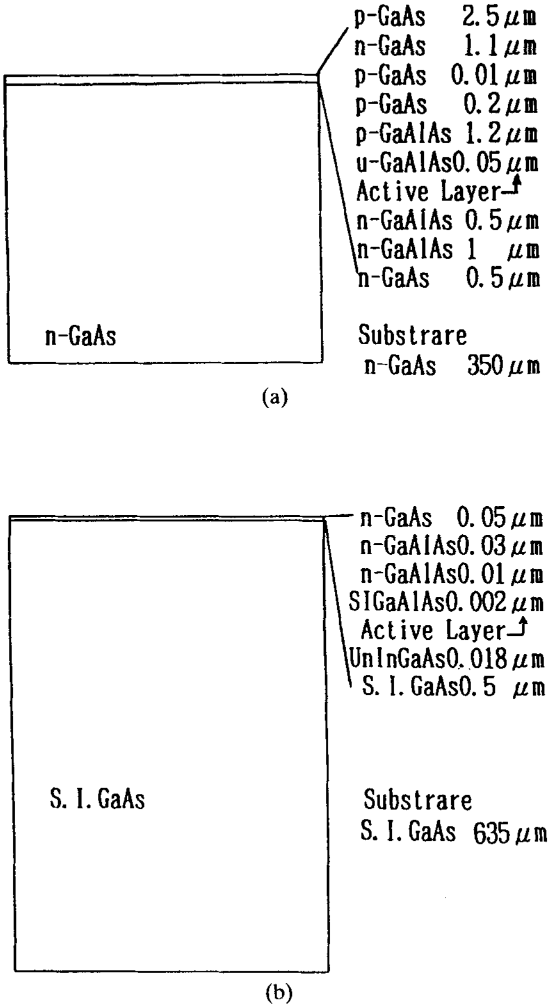

Figure 9 Structure of MO-CVD and MBE Epi wafers: (a) produced by MO-CVD; (b) produced by MBE.

method. As the many layers from under 1 μm to a few micrometers thick are grown by decomposing trimethyl gallium [$(CH_3)_3Ga$], arsine (AsH_3) and phosphine (PH_3) with heat under low pressure, MO-CVD Epi wafers for lasers can be produced. GaAs substrates are charged in the preparation chamber of the MO-CVD system in a high-grade clean room. The worker inputs data for gas flow rate, valve operation, heating, and vacuum, etc., at the control panel. After the preparation chamber has been evacuated, GaAs substrates are transferred in turn to the MO-CVD chamber, and heated with radio-frequency waves (microwaves). Many kinds of gases are passed into the chamber and decomposed, so that thin layers are grown gradually. After a fixed period, the MO-CVD Epi wafer is moved back to the preparation chamber, which is leaked to atmospheric pressure by nitrogen. These operations are performed automatically. The commercial MO-CVD system is always ventilated, while the worker charges and takes out the GaAs substrates. Gas leak detectors and exhaust ducts for safety are set in the MO-CVD system and clean room.

4.7 MBE method[11]

The principle of MBE is that gallium and arsenic molecules deposit on the GaAs substrate. The molecular beams are produced by heating gallium and arsenic under ultra-high vacuum. Gallium and arsenic are deposited on the surface of a GaAs substrate (Fig. 10), where the GaAs substrate is kept at a moderate temperature to absorb the kinetic energy of the beams. Very thin MBE Epi wafer layers are grown by deposition, because the layers can be controlled with a thickness analyzer. In practice, the worker charges gallium and arsenic in each oven, and the chamber is at ultra-high vacuum. The GaAs substrates are set in the preparation chamber in a high-grade clean room, and the chamber is evacuated. The GaAs substrates are transferred by remote control to an epitaxial growth bell jar. The GaAs substrates, gallium and arsenic are heated, and kept at a fixed temperature. The

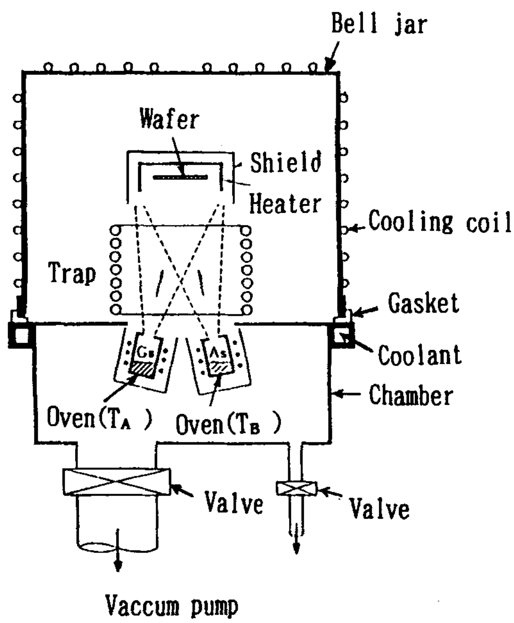

Figure 10 MBE system.

single-crystal layer is grown while the shutter is opened for a fixed period. The MBE Epi wafer is moved to the preparation chamber, which is leaked to normal pressure. Then, the MBE Epi wafers ar taken out.

5 WORKING CONDITIONS

The workers wear a clean mask, a clean hood, clean garments, and clean shoes for ensuring clean conditions in the VPE, LPE, MO-CVD, MBE, LEC, lapping, polishing, packing and inspection areas. Their garments and hoods are washed periodically. The GF and slicing workers put on a cap, and an upper garment which are also washed periodically. Workers in the LEC area put on an airline-type mask during cleaning. The cleaning place is always ventilated. After workers finish cleaning, they take a shower bath. The floors are cleaned every day. The state of cleanliness of all areas is checked monthly.

DISCUSSION

In middle-grade clean rooms (e.g. clean class 10 000), arsenic dust concentration is estimated at 0.0005 mg m^{-3}, even if all dust is around 1 μm diameter and is present as GaAs. This value is low.

All things considered, occupational disease in the GaAs plant should hardly be possible. It is certified that no occupational disease in the GaAs industry has been reported over 20 years. The weight of GaAs in an LED lamp is under 0.1 mg, and the lamp is covered with epoxy resin, which is stable and safe. There is little danger in using LED lamps in home electric goods nowadays. When the consumption volume of GaAs devices increases in future, their disposal will have to be considered.

Acknowledgement The authors express sincere thanks to Dr S. Ishigro, Furukawa Co. Ltd, for information on arsenic world production volume.

REFERENCES

1. L. J. Ungers, P. D. Moskowitz, T. W. Owens, A. D. Harmon and T. M. Briggs, *Am. Ind. Hig. Assoc. J.* **43**, 73 (1982).
2. H. Yamauchi, K. Takahashi, M. Mashiko and Y. Yamamura, *Am. Ind. Hig. Assoc. J.* **50**, 606 (1989).
3. T. A. Roshina, *Gig. Tr. Prof. Zabol.* **10**, 30 (1966).
4. S. Ishigro, *Appl. Organomet. Chem.* **6**, 323 (1992).
5. F. Orito, H. Fujita and T. Sato, *Japan J. Crystal Growth* **121**, 255 (1992).
6. T. Shimoda and S. Akai, *J. Appl. Phys.* **8**, 1352 (1969).
7. H. Okada, T. Katsumata, T. Obokata, T. Fukuda and W. Susaki, *J. Crystal Growth* **75**, 117 (1986).
8. J. W. Burd, *Trans. Met. Soc. AIME* **245**, 571 (1969).
9. H. Nelson, US patent 3 565 702 (1971).
10. H. M. Manasevit and W. I. Simpson, *J. Electrochem. Soc.* **116**, 1725 (1969).
11. A. Y. Cho and J. R. Arthur, *Prog. Solid State Chem.* **10**, 157 (1975).