PREPARATION OF GAP-SI HETEROJUNCTION BY LIQUID
PHASE EPITAXY
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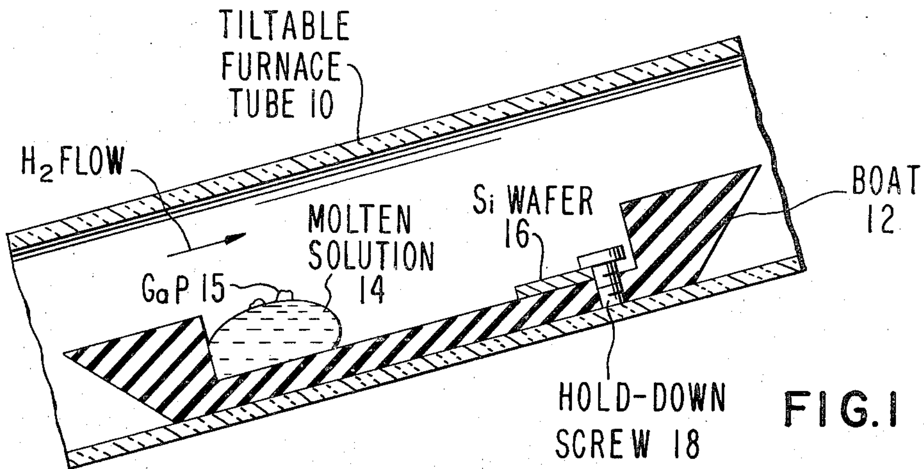

FIG. 1

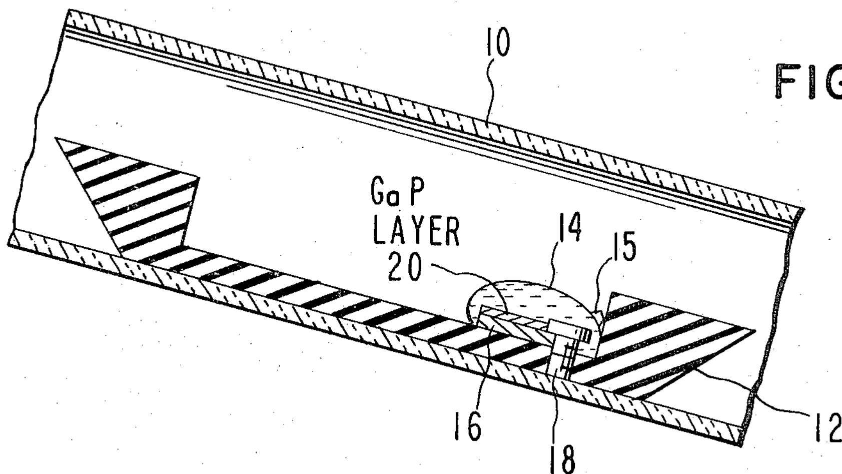

FIG. 2

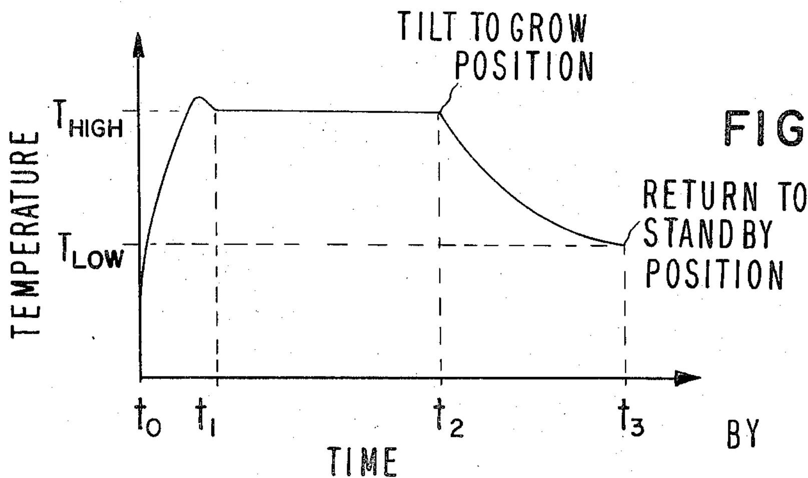

FIG. 3

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PREPARATION OF GaP-Si HETEROJUNCTION BY LIQUID PHASE EPITAXY

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ABSTRACT OF THE DISCLOSURE

A saturated molten solution of GaP and Si in a suitable solvent (Pb, Sn) was prepared. The molten, saturated solution was brought into contact with a Si single crystal substrate and cooled, causing the GaP to form an epitaxial layer on the Si surface. The crystal lattice structure and dimensions of Si and GaP crystals are very similar. The preferred physical properties of the solvent are: a relatively high solubility for GaP; a relatively low solubility for Si; and a relatively low solubility of the selected solvent in the epitaxially grown GaP.

FIELD OF THE INVENTION

This invention relates to the epitaxial growth of GaP on Si by liquid phase epitaxy and more particularly to the use of Pb and/or Sn as solvents for that purpose.

DESCRIPTION OF THE PRIOR ART

It is known to epitaxially deposit GaP onto Si by fused salt electrolysis as reported by J. J. Cuomo and R. J. Gambino, J. Electrochem. Soc: Vol. 115, page 755 (July 1968). Further, liquid phase epitaxy has been employed to produce heterojunctions such as Ge-Si as reported by K. Kurata and T. Hirai, J. Electrochem. Soc.: Vol. 115, page 869 (August 1968), and Ge on GaAs as reported by F. Rosztoczy, J. Electrochem. Soc: Vol. 115, page 328C (1968).

Gas phase heteroepitaxy has also been reported by Robert W. Thomas, J. Electrochem. Soc: Vol. 116, No. 10, (1969) wherein epitaxy of GaP on single crystal silicon was achieved using gallium and phosphorous alkyls.

Further hereteroepitaxial growth of GaP on single crystal silicon was achieved by Osamu Igaroshi as reported in Journal of Applied Physics, Vol. 41, page 3190 (1970), This technique involved the evaporation of the compound onto a suitably prepared silicon substrate.

SUMMARY OF THE INVENTION

It is therefore an object of this invention: to provide an improved technique for growing GaP on Si by liquid phase epitaxy; to provide a liquid phase epitaxy technique for growing GaP on Si using a carrier solvent; to provide a liquid phase epitaxy technique for growing GaP on silicon using Sn and/or Pb as a carrier solvent; and to provide an improved technique for manufacturing a semiconductor film on a low cost Si substrate.

BRIEF DESCRIPTION OF THE DRAWING

Further objects and advantages of the present invention and the method of growing GaP on Si will become apparent from the following detailed description taken in conjunction with the drawings in which:

FIG. 1 is a sectional view of a tiltable furnace tube in the standby position showing the saturated solution and the silicon substrate before contact;

FIG. 2 is a sectional view of the tiltable furnace in the growing position showing the saturated solution covering the Si substrate during epitaxy; and

FIG. 3 is a plot of temperature versus time depicting the thermal cycle employed by the apparatus of FIG. 1 and 2.

Referring to FIG. 1, there is shown a tiltable furnace tube **10** in a first or standby position, containing a boat **12**. Boat **12** is made of a refractory material, for example, graphite, BN, or quartz. A solution **14** of GaP and Si in a solvent is shown at the lower end of boat **12**. The solution is preferably saturated with GaP to expedite epitaxial growth later. Solution **14** is maintained in the molten state by a furnace (not shown). Excess GaP **15** on solution **14** assures that the solution is saturated. A Si wafer or substrate **16** is mounted at the upper end of boat **12** by means of a refractory hold down screw **18** which is also a refractory material. It is preferable that Si substrate **16** be a single crystal having a crystal orientation of (111) or (100). A flow of inert gas, preferably H_2, is maintained through furnace tube **10** to prevent oxidation of molten solution **14**. Contact between solution **14** and substrate **16** is established by tilting furnace tube **10** into a second or growing position as shown in FIG. 2. Solution **14** rolls to the opposite end of furnace tube **10** and covers substrate **16** causing a GaP crystal **20** to form. The apparatus of FIG. 1 is similar in design to the H. Nelson apparatus described in RCSA Review, vol. 24, page 603 (1963). Clearly other types of solution-substrate contacting apparatus may be employed.

FIG. 3 depicts the thermal cycle employed in growing GaP layer **20** on substrate **16** using the apparatus of FIG. 1. From t_0 to t_1 the temperature is elevated with furnace tube **10** in the standby position. From time t_1 to time t_2 furnace is maintained at a preselected constant temperature T_{high} to melt the initial charge and form saturated solution **14**. At time t_2 furnace tube **10** is tilted into the growth position and solution **14** rolls across boat **12** and covers substrate **16**. The temperature is slowly decreased to T_{low} causing GaP to form an epitaxial layer onto substrate **16**. The lattice constant of GaP is 5.4505 and the lattice constant of Si is 5.43072, sufficiently matched to permit GaP to epitaxially grow on the surface of Si substrate **16**. At time t_3, furnace tube **10** is tilted back to the standby position causing solution **14** to return to its original position. The excess solution is removed from the surface of substrate **16** by a scraper apparatus (not shown).

The solvent or carrier material in saturated solution **14** may be formed by more than one material, and is selected on the basis of the following physical properties:

(1) Relatively low solubility coefficient for Si.—This limits the amount of Si that dissolves into the solution **14**. In this way the doping and other effects of silicon can be minimized.

(1) Relatively high solubility coefficient for GaP.—This permits the GaP to go into solution for epitaxial growth onto the substrate.

(2) Relatively high solubility coefficient for GaP.—This permits the GaP to go into solution for epitaxial growth onto the substrate.

(3) A low solubility coefficient into the GaP crystal which is being grown.—This limits the concentration of solvent included in the GaP crystal which minimized the doping effect of the solvent.

(4) Preferably removable by cleaning solvent such as HCl and HNO_3.—After the GaP-Si junction has been prepared, it may be desirable to clean the GaP surface to remove any carrier solvent which was not removed by scraping molten solution **14** in furnace tube **10**.

Pb solvent embodiment

Pb is a suitable solvent for the present technique. Pb has a low solubility coefficient for Si (about 0.1 mol percent at 950° C.) and a high solubility coefficient of GaP

(about 2 mol percent at 950° C.). In this embodiment saturated solution **14** was prepared by thoroughly mixing 13 grams of Pb and 0.3 gram of GaP. The amount of GaP is more than can be dissolved in 13 grams of Pb at the T_{high} involved which guaranteed that the solution was saturated. The mixture was placed in boat **12** and maintained at 950° C. for 60 minutes. A small portion of the GaP remained undissolved. The system was quenched and subsequently saturated with Si at 950° C. for 60 minutes to prevent Si substrate **16** from dissolving into solution **14** during the FIG. 2 contact step. The system was quenched again and Si substrate **16** was placed in boat **12** at the opposite end thereof from saturated solution **14**. The quenching steps are not shown in FIG. 3. The temperature of the system was raised to 950° C. (T_{high}) and maintained for 30 minutes. Furnace tube **10** was tilted into the growing position and solution **14** came in contact with substrate **16**. The temperature was dropped to 800° C. (T_{low}) over a period of 60 minutes. Furnace tube **10** was tilted back to the standby position. The resulting epitaxial layer **20** was approximately 10 microns thick.

T_{high} (in this case preferably 950° C.) is not critical and is a function of the solubility coefficients of the materials and the desired composition of solution **14**. Preferably solution **14** should be about 1% by weight of GaP. The concentration of GaP can be as low as .1% by weight, in which case the epitaxial growth proceeds very slowly. The concentration of GaP may be as high as 20% or even higher. At the high GaP concentrations, the epitaxial growth proceeds rapidly causing defects in the crystal lattice and incorporation of impurities from the solution. T_{low} (in this case preferably 800° C.) was selected on the basis of the required thickness of GaP layer **20**. Slower cooling rates tend to produce higher quality crystals, and of course avoid the possibility of constitutional super cooling. Subject to these considerations, the temperatures and cooling rate are not critical.

The time periods described above are representative of the time required for the solution to reach equilibrium without external agitation. Atomic diffusion was the primary means through which equilibrium was obtained. The time periods may be shortened considerably by agitating solution **14** or rocking boat **12**. In any event the time periods are not generally critical.

Sn solvent embodiment

Sn is also a suitable solvent having a relatively low solubility coefficient for Si and a relatively high solubility coefficient of GaP. A saturated solution of GaP in Sn was prepared by placing 5 grams of Sn and 0.5 gram of GaP in boat **12** (more than sufficient GaP for the temperature involved) and maintaining the temperature at 850° C. for a period of 60 minutes. Solution **14** was quenched and Si saturated as described in the Pb embodiment and brought into contact with substrate **16**. The temperature was lowered to 650° C. over a period of 3 hours, resulting in a 10 micron GaP layer epitaxially grown on Si.

If desired, the quenching steps can be eliminated by initially placing all of solution **14** constituents (GaP, Pb and/or Sn, Si) at the lower end of the boat in the standby position. Si substrate **16** is then mounted at the upper end of boat **12**. The temperature of the system is cycled only once as depicted in FIG. 3.

The resulting GaP-Si heterojunction has a low cost Si base. The price of the Si substrate is approximately 1000 times less than the price of suitable GaP substrates. The uncoated side of the Si substrate is also suitable for use as part of the integrated circuit employed in conjunction with the GaP layer.

Clearly various changes may be made in the structude and embodiments shown herein without departing from the concept of the present invention. In addition to the horizontal apparatus of FIGS. 1 and 2, a vertical structure may be employed wherein the substrate is dipped into the solution (see F. E. Rosztoczy, Varian Technical Journal, No. 3, page 1 (Spring 1970). Further a steady state-temperature gradient technique may be employed which does not employ a thermal cycle as depicted in FIG. 3. Instead, the substrate is maintained at a constant temperature slightly lower than the source of GaP causing a gradient across the solution.

What is claimed is:

1. In a method for forming a binary GaP layer on a Si substrate through liquid phase epitaxy comprising the steps of:

providing a solution of GaP in a solvent at a first temperature wherein the solvent is at least one element selected from the group consisting of Pb and Sn;
providing a suitable Si substrate;
establishing contact between the Si substrate and the solution; and
causing the GaP in solution to epitaxially form binary GaP over the Si substrate by lowering the temperature of at least that part of the solution proximate the substrate to a second temperature which is lower than the first temperature.

2. The method of claim **1** wherein the solvent is Pb.

3. The method of claim **2** wherein the first temperature is 950° C. and the second temperature is 800° C.

4. The method of claim **1** wherein the solvent is Sn.

5. The method of claim **4** wherein the first temperature is 850° C. and the second temperature is 650° C.

6. The method of claim **1** wherein the solution of GaP and solvent is saturated with GaP and the Si substrate is a single Si crystal.

7. The method of claim **6** wherein the solution of GaP and solvent is saturated with Si before contact with the Si substrate.

8. The method of claim **6** wherein the concentration by weight of GaP in the solution is from about 0.1% to about 20%.

9. The method of claim **6** wherein the concentration by weight of GaP in the solution is about 1%.

References Cited

UNITED STATES PATENTS

3,278,342 10/1966 John et al. .... 148—1.6

OTHER REFERENCES

Woodall, Growth of Ga_{1-x} in P_x on Si substrates, IBM Technical Disclosure Bulletin, vol. 12, No. 11, April 1970, p. 1834.

J. Electrochem. Soc., vol. 115, pp. 755–9, July 1968.

J. Electrochem. Soc., vol. 116, No. 10, pp. 1449–50.

Journal of Applied Physics, vol. 41, pp. 3190–2 (1970).

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