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[45] **Oct. 1, 1974**

[54] **MOLECULAR BEAM EPITAXY METHOD FOR FABRICATING MAGNESIUM DOPED THIN FILMS OF GROUP III(A)-V(A) COMPOUNDS**

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[52] **U.S. Cl.** ..... **117/215,** 117/106 A, 117/201, 148/175, 317/235 AQ, 317/235 N

[51] **Int. Cl.** **B44d 1/18**

[58] **Field of Search** ..... 148/175; 117/200, 201, 117/215, 217, 227, 107, 106 A; 317/235 AQ, 235 N

[56] **References Cited**

UNITED STATES PATENTS

3,615,931	10/1971	Arthur, Jr. et al.	148/175
3,751,310	8/1973	Cho	148/175

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[57] **ABSTRACT**

In a molecular beam epitaxy method of fabricating a Mg doped thin film of a compound of the form $Al_xB_{1-x}C$, where B is a Group III(a) element and C is a Group V(a) element, the sticking coefficient of magnesium is a nonlinear, monotonically increasing function of the amount of aluminum. P-type thin films of $Al_xB_{1-x}C$:Mg having a predetermined carrier concentration are fabricated by including in the molecular beam(s) an appropriate amount of aluminum determined from said function.

10 Claims, 2 Drawing Figures

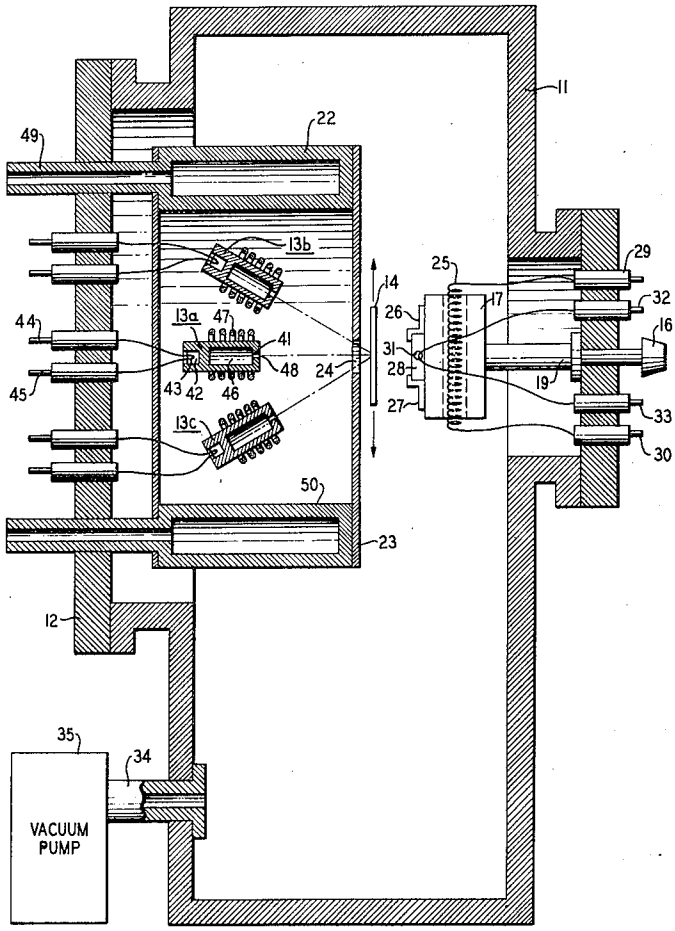


FIG. 1

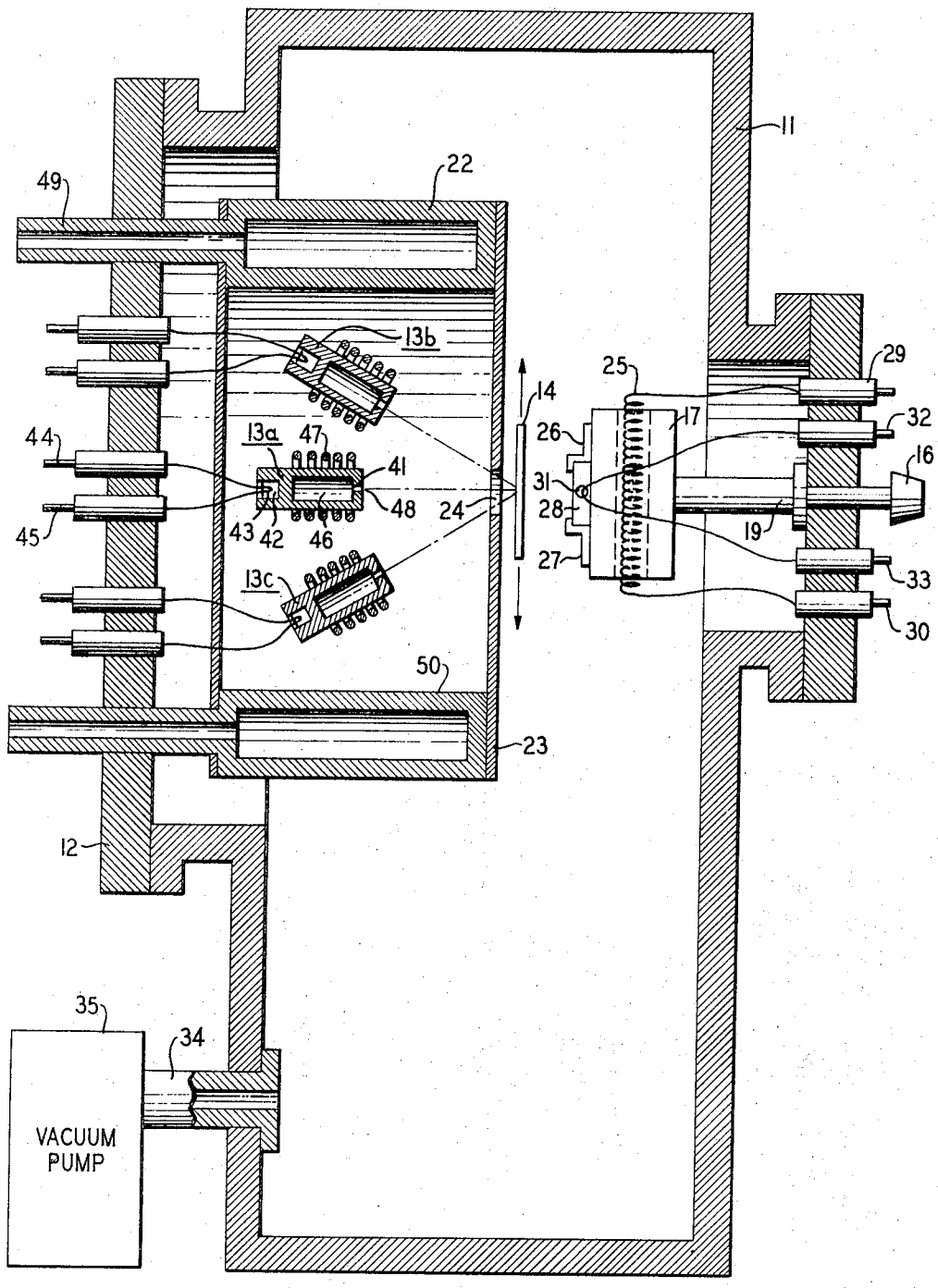
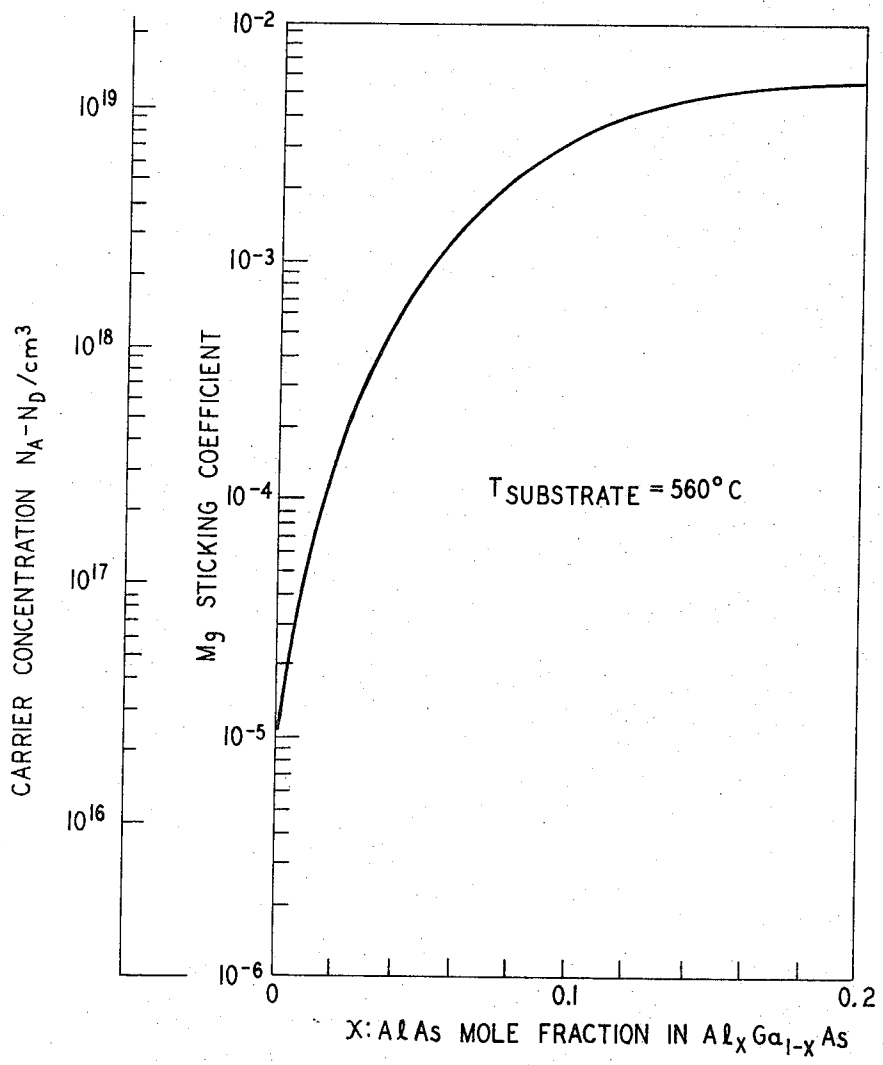

11
22
49
13b
14
25
29
44
13a
47
41
26
17
32
16
31
28
48
24
19
45
43
42
46
27
33
13c
30
50
23
12
35
34
VACUUM
PUMP

FIG. 2


CARRIER CONCENTRATION $N_A - N_D / cm^3$
10^{19}
10^{18}
10^{17}
10^{16}
Mg STICKING COEFFICIENT
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
$T_{SUBSTRATE} = 560°C$
0
0.1
0.2
X: AlAs MOLE FRACTION IN $Al_X Ga_{1-X} As$

MOLECULAR BEAM EPITAXY METHOD FOR FABRICATING MAGNESIUM DOPED THIN FILMS OF GROUP III(A)-V(A) COMPOUNDS

BACKGROUND OF THE INVENTION

This invention relates to the epitaxial growth of thin films of controllable thickness and, more particularly, to a molecular beam epitaxy technique for fabricating thin films of Group III(a)–V(a) compounds having p-type conductivity. The Group III(a) and Group V(a) elements referred to herein are those identified in the Chemical Rubber Handbook, Vol. 45, page B-2, published by the Chemical Rubber Company.

Molecular beam epitaxy (MBE), as described in U.S. Pat. 3,615,931 granted to J.R. Arthur, Jr. on Oct. 26, 1971 and assigned to the assignee hereof, is a comparatively new technique for the epitaxial growth of semiconductor materials, in which growth results from the simultaneous impingement of one or more molecular beams of the constituent elements onto a heated substrate. In MBE the growth process is governed primarily by kinetics whereas in liquid phase epitaxy or chemical vapor phase epitaxy growth is governed by near thermodynamic equilibrium conditions. In MBE, therefore, the incorporation of doping elements into the grown layers is strongly dependent on the arrival rate, the adsorption lifetime, and the condensation coefficient of the element on a particular substrate surface.

Unfortunately, desirable p-type dopants such as Zn and Cd have such low sticking coefficients on materials such as GaAs at the growth temperature (resulting from low condensation coefficients and/or low adsorption lifetimes) that the incorporation of these elements as useful dopants into GaAs during MBE growth has not been successful. However, as described by one of us, A. Y. Cho, in copending application Ser. No. 127,926 filed on Mar. 25, 1971 (now U.S. Pat. No. 3,751,310, issued on Aug. 7, 1973) and assigned to the assignee hereof, other elements having unity sticking coefficients such as Si, Ge, and Sn have been successfully used to dope layers grown by molecular beam epitaxy. Both Si and Sn are preferentially incorporated into GaAs as donors and therefore produce n-type layers. On the other hand, Ge forms n- or p-type layers depending on the surface configuration of the GaAs layer during growth. More specifically, Ge produces a p-type layer when the molecular beams are adapted to create during growth a relatively Ga-rich surface. Conversely, Ge produces an n-type layer when the molecular beams are adapted to create during growth a relatively As-rich surface. The conditions which must be varied to produce these two surfaces are the substrate temperature and the ratio of As_2/Ga in the molecular beams. The maintenance of a Ga-rich surface during MBE growth without formation of Ga droplets is, however, difficult because it requires relatively highly stable beam intensities (i.e., fluxes) for long periods of time.

Many of the uses of good quality, thin p-type layers are, of course, obvious, e.g., in the fabrication of p-n junction devices. The need for such layers has become significantly greater with the recent devleopment of the GaAs-AlGaAs double heterostructure (DH) junction laser, the only semiconductor laser at this time which is capable of c.w. operation at room temperature. The ability of some types of DH laser to operate c.w. at room temperature is dependent to a large extent upon the inclusion in the device of an active layer less than 1 μm thick. Thus, the fact that MBE permits reproducible growth of thin layers of controllable thickness less than 1 μm, renders this growth technique particularly suitable to the fabrication of the thin GaAs-AlGaAs layers of the DH laser. However, there is still a need for a technique for incorporating a p-type dopant into MBE layers of compounds of the form $Al_xB_{1-x}C$, where Al is aluminum, B is a Group III(a) element and C is a Group V(a) element. To avoid the formation of Ga droplets previously mentioned, it is preferred that the p-type dopant be incorporated while maintaining a surface condition which is stabilized in the Group V(a) element (e.g., an As-rich surface condition when growing AlGaAs layers).

Atoms of a Group II element usually enter the lattice of a III(a)–V(a) compound by substituting for atoms of the Group III(a) element to give acceptor centers. However, as already mentioned, we have been unsuccessful in our attempts to incorporate useful amounts of Zn and Cd, for example, into GaAs by the MBE method. On the other hand, we have been able to incorporate relatively small amounts of Mg as a p-type dopant in GaAs only by using a relatively high Mg beam flux (e.g., an arrival rate of 10^{14}/cm^2 sec) to compensate for its low sticking coefficient (about 10^{-5} at 560° Centigrade). Evan at high beam fluxes, however, the carrier concentration of the grown layers is only about 10^{16}/cm^3, whereas in many devices (e.g., the p-type active region of a double heterostructure laser) it is preferable that the carrier concentration be about 5×10^{17} to 5×10^{18}/cm^3.

Summary of the Invention

During the process of growing MBE layers of $Al_xGa_{1-x}As$ doped with Mg, we have discovered that the sticking coefficient of magnesium, and hence the carrier concentration of the layers, increases monotonically with x, the mole fraction of AlAs in $Al_xGa_{1-x}As$. More specifically, for an illustrative substrate temperature of about 560° Centigrade, we have found that as aluminum is added to the grown layer so that x increases from 0 to 0.2, the sticking coefficient of Mg rapidly increases by nearly three orders of magnitude from about 10^{-5} to about 10^{-2}. Correspondingly, the carrier concentration of the grown layers increases from about 10^{16}/cm^3 to about 10^{19}/cm^3. Concentrations of 5×10^{17}/cm^3 to 5×10^{18}/cm^3 are attained with x in the range 0.02 to 0.08 approximately.

The increase by three orders of magnitude in the sticking coefficient of Mg and therefore the increase in the carrier concentration in the grown layers has several important implications. First, we have been able to grow p-type MBE layers having carrier concentrations in the 10^{18}/cm^3 range which are suitable for double heterostructure junction lasers, whereas priorly the maximum Mg doping level attained was only 10^{16}/cm^3. Moreover, the amount of aluminum ($x = 0.02$ to 0.08) to produce the higher concentrations is also suitable for creating in a DH laser the necessary refractive index steps which, as in now well known, produce both optical and carrier confinement.

Secondly, the ability to vary the sticking coefficient of Mg by controlling the intensity of the Al beam (i.e., the Al arrival rate) means that, for a given carrier concentration in the layer grown, a lower Mg beam flux

may be used by increasing the amount of Al in the layer, i.e., by increasing the intensity of the Al beam.

Looked at in another way, the latter feature of our invention permits fabrication of MBE multilayered devices in a controlled fashion. Consider, for example, that one skilled in the art desires to grow by MBE contiguous layers of *p*-type GaAs and *p*-type $Al_{0.1}Ga_{0.9}As$ both doped with Mg and both having the same carrier concentration. Ordinarily, one would adjust the Mg beam to produce a predetermined, but fixed, arrival rate. To his chagrin, the worker would find that the carrier concentration of the GaAs:Mg layer was only about $10^{16}/cm^3$ whereas that in the $Al_{0.1}Ga_{0.9}As$ layer was about $10^{19}/cm^3$. Our discovery, on the other hand, indicates that for $x = 0.1$ the Mg sticking coefficient is nearly three orders of magnitude higher than for $x = 0$ (i.e., pure GaAs). Consequently, when growing the $Al_{0.1}Ga_{0.9}As$ layer, the Mg beam should be adjusted to produce an arrival rate three orders of magnitude smaller.

Brief Description of the Drawing

Our invention, together with its various features and advantages, can be easily understood from the following more detailed description taken in conjunction with the accompanying drawing, in which:

FIG. **1** is a partial cross-sectional view of illustrative apparatus utilized in practicing our invention; and

FIG. **2** is a graph of carrier concentration and Mg sticking coefficient versus AlAs mole fraction in $Al_xGa_{1-x}As$.

DETAILED DESCRIPTION

Apparatus

Turning now to FIG. **1**, there is shown apparatus for growing by MBE epitaxial films of Group III(*a*)–V(*a*) compounds, and mixed crystals thereof, of controllable thickness and conductivity type.

The apparatus comprises a vacuum chamber **11** having disposed therein a gun port **12** containing illustratively three cylindrical guns **13***a*, **13***b* and **13***c*, typically Knudsen cells, and a substrate holder **17**, typically a molybdenum block. In FIG. **1** the guns **13** are shown to be disposed in a vertical plane for clarity of illustration. Holder **17** is adapted for rotary motion by means of shaft **19** having a control knob **16** located exterior to chamber **11**. Also shown disposed within chamber **11** is a cylindrical liquid nitrogen cooling shroud **22** which surrounds the guns and a collimating frame **23** having a collimating aperture **24**. Substrate holder **17** is provided with an internal heater **25** and with clips **26** and **27** for affixing a substrate member **28** thereto. Additionally, a thermocouple is disposed in aperture **31** in the side of substrate **28** and is coupled externally via connectors **32–33** in order to sense the temperature of substrate **28**. Chamber **11** also includes an outlet **34** for evacuating the chamber by means of a pump **35**.

A typical cylindrical gun **13**a comprises a refractory crucible **41** having a thermocouple well **42** and a thermocouple **43** inserted therein for the purpose of determining the temperature of the material contained in the gun source chamber **46**. thermocouple **43** is connected to an external detector (not shown) via connectors **44–45**. Source material (e.g., bulk GaAs) is inserted in source chamber **46** for evaporation by heating coil **47** which surrounds the crucible. The end of crucible **41** adjacent aperture **24** is provided with a knife edge opening **48** (typically about $0.17cm^2$) having a diameter preferably less than the average mean free path of atoms in the source chamber.

General MBE Technique

The first step in a typical MBE technique involves selecting a single crystal substrate member, such as GaAs, which may readily be obtained from commerical sources. One major surface of the GaAs substrate member is initially cut along the (001) plane and polished with diamond paste, or any other conventional technique, for the purpose of removing the surface damage therefrom. An etchant such as a bromine-methanol or hydrogen peroxide-sulphuric acid solution may be employed for the purpose of further purifying the substrate surface subsequent to polishing.

Next, the substrate is placed in an apparatus of the type shown in FIG. **1**, and thereafter, the background pressure in the vacuum chamber is reduced to less than 10^{-6} Torr and preferably to a value of the order of about 10^{-8} to 10^{-10} Torr, thereby precluding the introduction of any deleterious components onto the substrate surface. Since, however, the substrate surface may be subject to atmospheric contamination before being mounted into the vacuum chamber, the substrate is preferably heated, e.g., to about 600° Centigrade, to provide an automically clean growth surface, (i.e., desorption of contaminants such as CO and H_2O). The next steps in the process involve introducing liquid nitrogen into the cooling shround via entrance port **49** and heating the substrate member to the growth temperature which typically ranges from about **450** to **650** degrees Centigrade dependent upon the specific material to be grown, such range being dictated by considerations relating to arrival rates and surface diffusion.

The guns **13***a*, **13***b* and **13***c* employed in the system have previously been filled with the requisite amounts of the constituents of the desired film to be grown (e.g., gun **13***a* contains a Group III(*a*)–V(*a*) compound such as a GaAs in bulk form; gun **13***b* contains a Group III(*a*) element such as Ga; and gun **13***c* contains a dopant such as Mg in bulk form). In the practice of our present invention, a fourth gun (not shown) containing Al is also used. Following, each gun is heated to a temperature (not necessarily all the same) sufficient to vaporize the contents thereof to yield (with shutter **14** open) a molecular beam (or beams); that is, a stream of atoms manifesting velocity components in the same direction, in this case toward the substrate surface. The atoms or molecules reflected from the surface strike the interior surface **50** of the cooled shroud **22** and are condensed, thereby insuring that only atoms or molecules from the molecular beam impinge upon the substrate surface.

For the purpose of the present invention, the amount of source materials (e.g., Ga, Al and GaAs) furnished to the guns and the gun temperatures should be sufficient to provide an excess of the Group V(*a*) element (As) with respect to the Group III(*a*) elements (Al and Ga); that is, the surface should be As-rich (also referred to as As-stabilized). This condition arises from the large differences in sticking coefficient at the growth temperature of the several materials; namely, unity for Ga and Al and about 10^{-2} for As_2 on a GaAs surface, the latter increasing to unity when there is an excess of Ga (and/or Al) on the surface. Therefore, as long as the As_2 arrival rate is higher than that of Ga

and/or Al, the growth will be stoichiometric. Similar considerations apply to Ga and P_2 beams impinging, for example, on a GaP substrate.

Growth of the desired doped epitaxial film is effected by directing the molecular beam generated by the guns at the collimating frame **23** which functions to remove velocity components therein in directions other than those desired, thereby permitting the desired beam to pass through the collimating aperture **24** to effect reaction at the substrate surface. Growth is continued for a time period sufficient to yield an epitaxial film of the desired thickness. This technique permits the controlled growth of films of thickness ranging from a single monolayer (about 3 Angstroms) to more than 100,000 Angstroms. Note, that the collimating frame serves also to keep the vacuum system clean by providing a cooled surface on which molecules reflected from the growth surface can condense. If the effusion cell provides sufficient collimation of the beams, however, the collimating frame is not essential to the growth technique.

The reasons which dictate the use of the aforementioned temperature ranges can be understood as follows. It is now known that Group III(*a*)–V(*a*) elements, which are adsorbed upon the surface of single crystal semiconductors, have different condensation and sticking coefficients as well as different adsorption lifetimes. Group V(*a*) elements typically are almost entirely reflected in the absence of III(*a*) elements when the substrate is at the growth temperature. However, the growth of stoichiometric III(*a*)–V(*a*) semiconductor compounds may be effected by providing vapors of Group III(*a*) and V(*a*) elements at the substrate surface, an excess of Group V(a) element being present with respect to the III(*a*) elements, thereby assuring that the entirety of the III(*a*) elements will be consumed while the nonreacted V(*a*) excess is reflected. In this connection, the aforementioned substrate temperature range is related to the arrival rate and surface mobility of atoms striking the surface, i.e., the surface temperature must be high enough (e.g., greater than about **450** degrees Centigrade) that impinging atoms have enough thermal energy to be able to migrate to favorable surface sites (potential wells) to form the epitaxial layer. The higher the arrival rate of these impinging atoms, the higher must be the substrate temperature. On the other hand, the substrate surface temperature should not be so high (e.g., greater than about 650 ° Centigrade) that noncongruent evaporation results. As defined by C. D. Thurmond in Journal of Physics Chem. Solids, 26, 785 (1965), noncongruent evaporation is the preferential evaporation of the V(*a*) elements from the substrate eventually leaving a new phase containing primarily the III(*a*) elements. Generally, therefore congruent evaporation means that the evaporation rate of the III(*a*) and V(*a*) elements are equal. The temperatures of the cell containing the III(*a*) element and the cell containing the III(*a*)–V(*a*) compound, which provides a source of V(*a*) molecules, are determined by the desired growth rate and the particular III(*a*)–V(*a*) system utilized.

Example: Doping AlGaAs with Mg

This example describes a process for the growth by MBE of p-type layers of $Al_xGa_{1-x}As$ doped with Mg.

In guns **13***a*, **13***b* and **13***c* there were placed, respectively, 1 gram of Al, 3 grams of polycrystalline GaAs and 3 grams of Ga. In a fourth gun (not shown for simplicity) was placed 0.5 gram of Mg. Each of the guns was made from aluminum oxide lined with spectroscopically pure graphite except for the Al gun which was made from pyrolytic BN in order to reduce the likelihood of aluminum oxides forming.

The vacuum in the chamber of FIG. **1**, was reduced to about 5×10^{-8} Torr which is primarily As_2 background pressure.

Next, the substrate **28**, comprising Si-doped *n*-type GaAs with its (001) surface facing the guns, was placed about 5cm from the guns and was heated to about 560° Centigrade. The latter temperature was chosen because layers grown at 560° Centigrade have exhibited higher photoluminescent (PL) efficiency than layers grown at other temperatures in the range 450° to 650° Centigrade. High PL efficiency is one of the prerequisites for the active region of a DH laser.

The guns were then heated to a suitable temperature effective to produce desired arrival rates at the growth surface. Thus, the Al gun **13***a* was heated to temperatures ranging from about 1200° to 1400° Kelvin to produce Al arrival rates ranging from about 10^{13} to 10^{15} Al/cm^2 sec; the GaAs gun **13***b* was heated to about 1180° Kelvin to produce an As_2 arrival rate of about 5×10^{15} As_2/cm^2 sec; the Ga gun **13***c* was heated to about 1,250° Kelvin to produce a Ga arrival rate of about 10^{15} Ga/cm^2 sec; and the Mg gun (not shown) was heated to about 680° Kelvin to produce a Mg arrival rate of about 10^{14} Mg/cm^2 sec.

With constant temperatures maintained for the Ga and GaAs guns as specified above, we fabricated a multilayered structure on the GaAs substrate to determine the doping profile in the several layers. The temperature of the Mg gun was the same for all layers except in two layers where Mg was omitted altogether. The temperature of the Al gun was changed from one layer to the next, but was constant during the growth of each particular layer. Eight layers were sequentially grown as follows with the temperatures in parenthesis being the Al gun temperature: (1) GaAs:Mg (850° Kelvin which produces negligible evaporation of Al) (2) $Al_{0.2-0}Ga_{0.80}As$: Mg (1,340° Kelvin); (3) $Al_{0.10}Ga_{0.90}As$: Mg (1,325° Kelvin); (4) $Al_{0.04}Ga_{0.96}As$: Mg (1,270° Kelvin); (5) $Al_{0.02}Ga_{0.98}As$: Mg (1,225° Kelvin); (6) $Al_{0.0-1}Ga_{0.99}As$: Mg (1,200° Kelvin); (7) GaAs: Mg (Al gun unheated); and (8) GaAs: undoped (Al gun unheated).

Several single-layered structures were also grown on Cr-doped semi-insulating GaAs substrates for the purpose of marking Hall effect measurements. All of the layers of the latter structure were grown with constant Mg, Ga and As_2 beam fluxes, but with varying Al beam intensities.

The epitaxial film properties were studied *in situ* with a reflection high energy electron diffraction (HEED) system commercially available from Varian Associates, Palo Alto, California and by Auger spectroscopy with a PHI cylindrical mirror electron spectrometer commercially available from physical Electronic Industries, Inc., Edina, Minnesota. Subsequent to growth, tests were also made with ion sputtering mass spectrometry (IMS) and Hall measurements. The arrangement of the *in situ* analysis instruments in the vacuum system of FIG. **1** is well known in the art and is therefore omitted here for simplicity and clarity of illustration.

HEED was used to observe the surface structures of the outermost atomic layers during growth. We ob-

served a new surface structure, GaAs (001) – 2×2 –Mg when the Mg beam was used to dope the various epitaxial layers. As the Mg beam impinged on a GaAs or $Al_xGa_{1-x}As$ surface, the (001) – 2×2 —Mg surface structure was formed independent of whether the initial surface was As-stabilized or Ga-stabilized.

Auger electron spectroscopy was used *in situ* to study the elemental composition of the top few monolayers of the grown epitaxial layers. this technique can be used to determine the substrate cleanliness, contamination (if any) of the layers during growth, and, to some extent, the chemical compositions of the $Al_xGa_{1-x}As$ layers.

IMS was used to determine the doping profile of the multi-layer structure and Hall effect measurements were used to determine the carrier concentrations and mobilities in the layers. The room temperature Hall mobilities varied from 215 cm^2/V sec for a carrier concentration $(N_A-N_D) = 2.5\times10^{16}/cm^3$ to 30 cm^2/V sec for $(N_A-N_D) = 10^{19}/cm^3$. Since the Mg beam flux was kept constant during the growth of the layers on the Cr-doped substrate, we conclude that the increase in carrier concentration corresponds to an increase in the sticking coefficient of Mg brought about by the presence of Al in the layers.

The results of our work are summarized in FIG. **2**, a graph of carrier concentration (N_A-N_D) and Mg sticking coefficient versus x, the mole fraction of AlAs in $Al_xGa_{1-x}As$. Although the data presented in FIG. **2** correspond to a substrate temperature of **560** degrees Centigrade, we expect similar results within the typical range of substrate temperatures suitable for epitaxial growth by MBE (i.e., about 450° to 650° Centigrade). The graph vividly depicts the drastic (three orders of magnitude) increase in Mg sticking coefficient from about 1×10^{-5} to 4×10^{-3} as the amount of aluminum in the grown layers (i.e., the mole fraction x) increases from about 0 to 0.1. The corresponding increase in carrier concentration is from about $2.5\times10^{16}/cm^3$ to about $8\times10^{18}/cm^3$. For x between 0.1 and 0.2 the increase is much more gradual: the sticking coefficient increases to about 6×10^{-3} and the corresponding carrier concentration increases to about $1.5\times10^{19}/cm^3$.

As mentioned previously, there are several ramifications of FIG. **2** which are important to the fabrication of devices by MBE.

First, we have demonstrated that Mg incorporates into MBE layers as a *p*-type dopant under As-stabilized surface conditions. Consequently, larger spurious variations of the As_2/Ga ratio in the molecular beams can be tolerated without seriously affecting the Mg doping level. Moreover, because growth on a Ga-stabilized surface is not necessary to obtain *p*-type conductivity (contrast the Ge situation), the likelihood that Ga droplets will form on the surface and disrupt the homogeneity of the layers is substantially reduced.

Secondly, we have demonstrated that the addition of aluminum to the molecular beam drastically increases the sticking coefficient of Mg and consequently the carrier concentration of the p-type layers grown. We can fabricate Mg doped AlGaAs layers with carrier concentrations as high as $10^{19}/cm^3$ whereas only about $10^{16}/cm^3$ was attainable priorly. P-type layers doped in the 5×10^{17} to $5\times10^{18}/cm^3$ range find important application in many semiconductor devices. A device of particular significance is the double heterostructure (DH) junction laser. Illustratively, the DH laser comprises an *n*-type GaAs substrate on which are grown sequentially the following layers: a n-$Al_xGa_{1-x}As$ layer; a p-$Al_yGa_{1-y}As$ layer and a p-$Al_zGa_{1-z}As$ layer with $y < x$ and z. The middle layer of $Al_yGa_{1-y}As$ forms the active region of the device where radiative recombination of holes and electrons occurs to produce a coherent light output. For efficient recombination to occur the carrier concentration is typically about $10^{18}/cm^3$. The condition $y < x$ and z creates a pair of heterojunctions at the interfaces with the middle layer. These heterojunctions confine injected carriers and optical photons to the middle layer and enable c.w. operation at room temperature if the thickness of the middle layer is less than about 1 μm. To this end, the other layers should also be thin (e.g., 1–2 μm) in order to facilitate the extraction of heat from the device.

Consequently, MBE, with its ability to grow extremely thin layers of controllable thickness, is particularly suited to the fabrication of DH lasers. As discussed in the copending application of A. Y. Cho (Case **2**) supra, Sn or Si may be used in MBE to produce the n-type $A1_xGa_{1-x}As$ layer in which typically $x = 0.1$. In accordance with one aspect of our invention, the layers of $Al_yGa_{1-y}As$ and $Al_zGa_{1-z}As$ can be made p-type by doping with Mg, and a predetermined carrier concentration in each can be attained by controlling the amount of Al incorporated into the layers, i.e., by controlling the temperature of the Al and Mg guns during MBE growth.

Thus, for example, to enhance photoluminescent efficiency the substrate is maintained at about 560° Centigrade. To produce a carrier concentration of about $1.5\times10^{18}/cm^3$ in the middle layer, the Al content should be about $y = 0.04$ which is attained when the Al gun is heated to about **1,270°** Kelvin. With the Mg gun heated to a suitable temperature sufficient to evaporate Mg molecules (e.g., to 680° Kelvin), a *p*-type $Al_{.04}Ga_{.96}As$:Mg layer about 1 μm thick is formed after about 60 minutes of growth time. Thinner layers may be fabricated by growing for shorter periods of time (growth is readily terminated by sliding the shutter 14 in front of aperture **24** of collimating frame **23**).

A fourth aspect of our invention relates again to our discovery that in Mg doped layers the carrier concentration is a function of the amount of Al in the layer. Thus, where it is desired to grow successive (not necessarily contiguous) layers of AlGaAs, for example, having different amounts of Al but the same carrier concentration, then the Mg beam flux must be adjusted to compensate for the changed Mg sticking coefficient. Illustratively, in the *n-p-p* DH laser discussed above, it might be desired that the p-$Al_{.04}Ga_{.96}As$ middle layer (y =0.04) and the p- $Al_{.10}Ga_{.90}As$ outer layer (z =0.10) have the same carrier concentrations, e.g., about $1.5\times10^{18}/cm^3$. But $y = 0.04$ produces a Mg sticking coefficient of about 6×10^{-4} whereas $x = 0.10$ produces a coefficient of about 3×10^{-3}, five times higher. Consequently, when growing the p-$Al_{.10}Ga_{.90}As$ layer the temperature of the Mg gun should be lowered to produce a Mg arrival rate about five times smaller than that used for growing the p-$Al_{.04}Ga_{.96}As$ layer.

It is to be understood that the above-described arrangements are merely illustrative of the many possible specific embodiments which can be devised to represent application of the principles of our invention. Numerous and varied other arrangements can be devised in accordance with these principles by those skilled in

the art without departing from the spirit and scope of the invention. In particular, although in the last-mentioned aspect of our invention the Mg flux was adjusted to produce the same carrier concentration in contiguous p-type layers of AlGaAs, it is of course apparent to one skilled in the art that our technique is generally applicable to producing different carrier concentrations by predetermining the requisite Al content and/or Mg beam intensity. Moreover, our invention is not limited in its application to AlGaAs only, but is also suitable to other III(a)–V(a) compounds containing Al, e.g., AlGaP, a material particularly attractive for use in GaP-AlGaP spontaneously emitting heterostructure diodes (LEDs).

What is claimed is:

1. A method for epitaxially growing upon a surface a p-type thin film of a material having a composition $Al_xB_{1-x}C$, where $0 < x \leq 1$, Al is aluminum, B is a Group III(a) element and C is a Group V(a) element, comprising the steps of:

a. reducing the background pressure to a subatmospheric pressure;

b. directing at least one molecular beam comprising a p-type dopant, said aluminum, said Group III(a) element and said Group V(a) element, upon said surface for a time period sufficient to effect growth of a p-type film of $Al_xB_{1-x}C$, $0 < x \leq 1$, of the desired thickness;

c. preheating said surface to a temperature effective to allow atoms impinging thereon to migrate to surface sites to form said epitaxial film and effective to produce congruent evaporation of said Group III(a) elements and said Group V(a) element:

d. maintaining the relative proportions of the constituents of said at least one molecular beam so that at said surface there is an excess of said Group V(a) element with respect to aluminum and said Group III(a) element, and characterized in that:

1. said p-type dopant is magnesium;

2. the sticking coefficient of magnesium on said surface, and hence the carrier concentration of said thin film, increases in accordance with a determinable relationship with increasing amounts of aluminum in said thin film; and

3. aluminum is included in said at least one molecular beam in an amount determined from said relationship effective to produce a desired carrier concentration in said thin film.

2. The method of claim **1** wherein said background pressure is reduced to at least 10^{-8} Torr.

3. The method of claim **1** wherein a first layer containing a first amount of Al is grown on said surface with the Mg flux in said at least one beam maintained at a first level, then a second layer containing a second amount of Al is grown, and during the growth of said second layer the Mg flux is changed to compensate for the change in the Mg sticking coefficient produced by the different amounts of Al in said layers.

4. The method of claim **1** wherein said surface is preheated to a temperature in the range of about 450° to 650° Centigrade.

5. The method of claim **4** wherein said thin film comprises a material selected from the group consisting of $Al_xGa_{1-x}As$ and $Al_xGa_{1-x}P$.

6. The method of claim **5** wherein said thin film comprises $Al_xGa_{1-x}As$ and said at least one molecular beam is formed by heating a first source of liquid Ga to produce a first beam of Ga molecules, by heating a second source of solid Al to produce a second beam of Al molecules, by heating a third source of As to produce a third beam of As molecules and by heating a fourth source of Mg to produce a fourth beam of Mg molecules, said first, second, third and fourth beams impinging simultaneously on said surface.

7. The method of claim **6** wherein said third source comprises polycrystalline GaAs to produce said third beam comprising As_2 molecules.

8. The method of claim **6** wherein the sticking coefficient of said Mg molecules on said surface increases according to said determinable relationship from about 10^{-5} to about 10^{-2} as the amount x of Al in said thin film increases from about 0 to 0.1 and produces a corresponding increase in the carrier concentration of said thin film from about $10^{16}/cm^3$ to $10^{19}/cm^3$.

9. The method of claim **6** wherein said thin film is made to have a carrier concentration greater than about $5\times10^{17}/cm^3$ by adapting the intensity of said aluminum beam to produce a thin film of $Al_xGa_{1-x}As$ with x greater than about **0.04.**

10. The method of claim **9** wherein said second source of Al is heated to a temperature greater than about 1,270° K.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,839,084 Dated October 1, 1974

Inventor(s) Alfred Yi Cho and Morton B. Panish

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 28, change "Evan" to --Even--.

Column 2, line 62, change "in" to --is--.

Column 4, line 21, change "10-8" to --10^{-8}--.

Column 4, line 64, change "10-2" to --10^{-2}--.

Signed and sealed this 31st day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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