

[54] **METHOD OF TRANSPORTING  
SUBSTANCES IN A PLASMA STREAM TO  
AND DEPOSITING IT ON A TARGET**

[75] Inventor: **Takashi Tsuchimoto**, Kodaira, Japan

[73] Assignee: **Hitachi, Ltd.**, Japan

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[21] Appl. No.: **254,902**

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[30] **Foreign Application Priority Data**

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|--------------|-------|----------|
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| May 21, 1971 | Japan | 46-34631 |
| May 21, 1971 | Japan | 46-34632 |

[52] **U.S. Cl.** ..... 427/38; 148/175; 313/154;  
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427/47; 156/614

[51] **Int. Cl.<sup>2</sup>** C23C 11/08; B05D 1/34; B05D 1/38;  
B05D 5/12

[58] **Field of Search** ..... 117/93.3, 93.2, 207, 217,  
117/93.1 GD, 106 A, 93; 250/492; 313/62,  
153, 154, 155; 315/111; 204/164, 165;  
148/175

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*Primary Examiner*—John Newsome

*Attorney, Agent, or Firm*—Craig & Antonelli

[57]

**ABSTRACT**

A method of transporting substances in plasma streams to and depositing them on a target in which the vapors of two or more selected materials are turned into separate ionized plasmas in separate plasma generating chambers, the plasmas are effused from their respective chambers due to the difference in plasma density between the inside and outside of the chamber to form separate plasma streams and the plasma streams are joined to form a single stream which is conducted to the surface of a substrate by means of axial magnetic fields which also serve to converge the plasma streams. In another embodiment, a single stream is branched by a magnetic field to form plural streams which are conducted to different substrates or different points on the same substrate.

**54 Claims, 17 Drawing Figures**

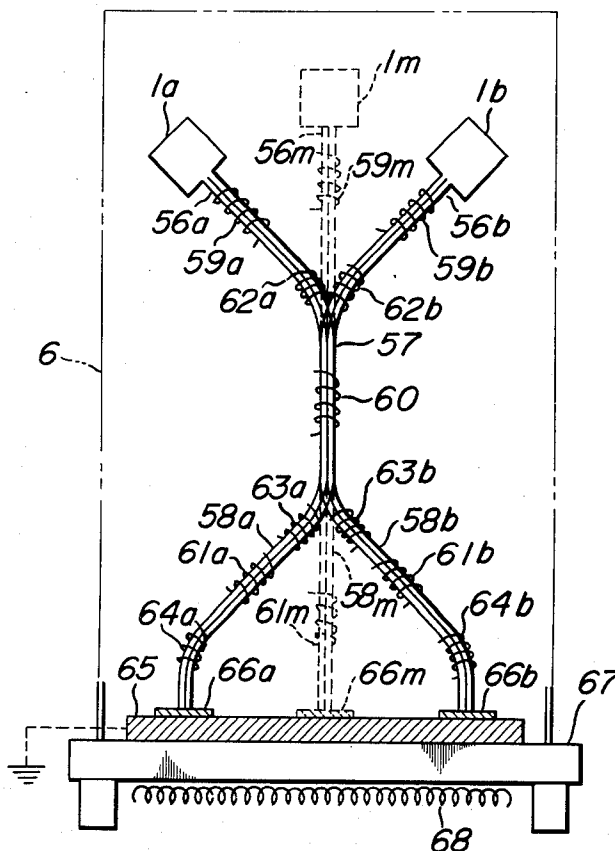


FIG. 1

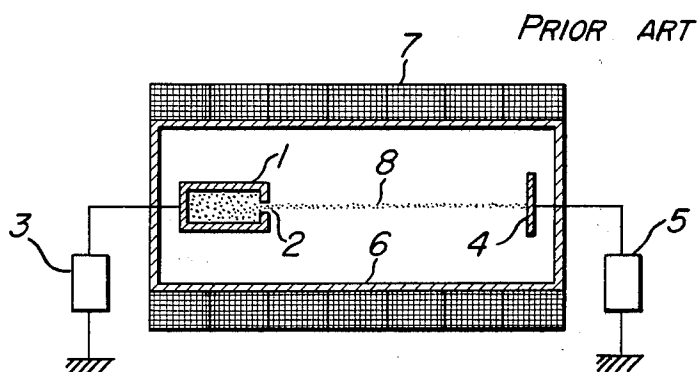


FIG. 2

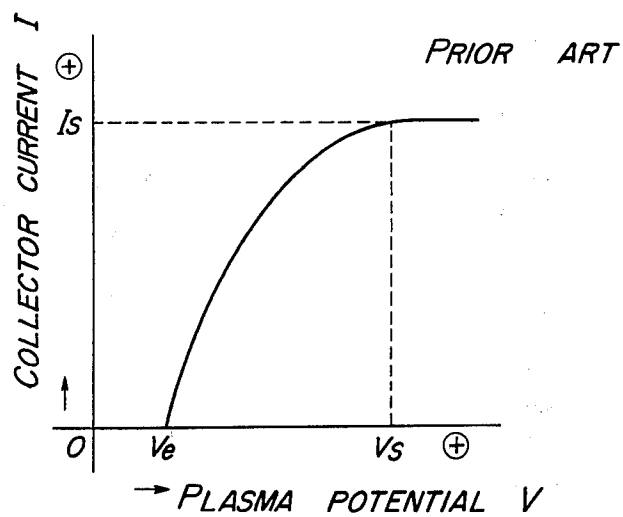


FIG. 3

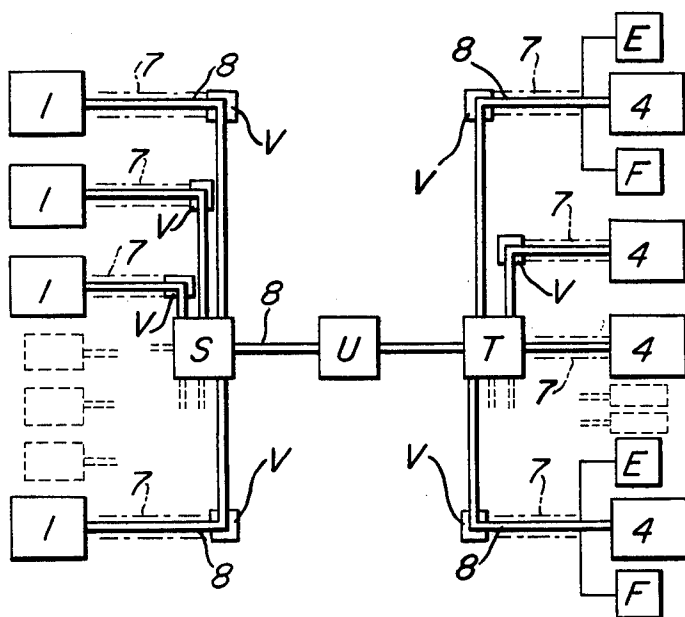


FIG. 4

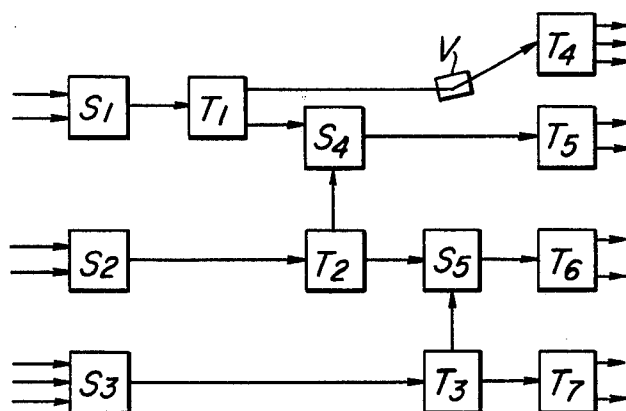


FIG. 5

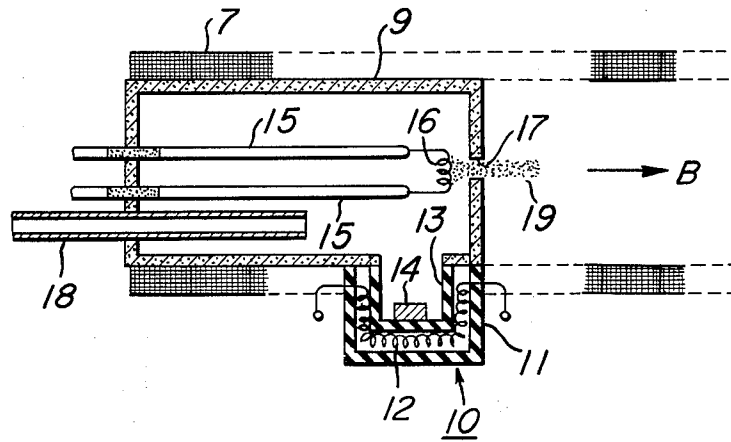


FIG. 6

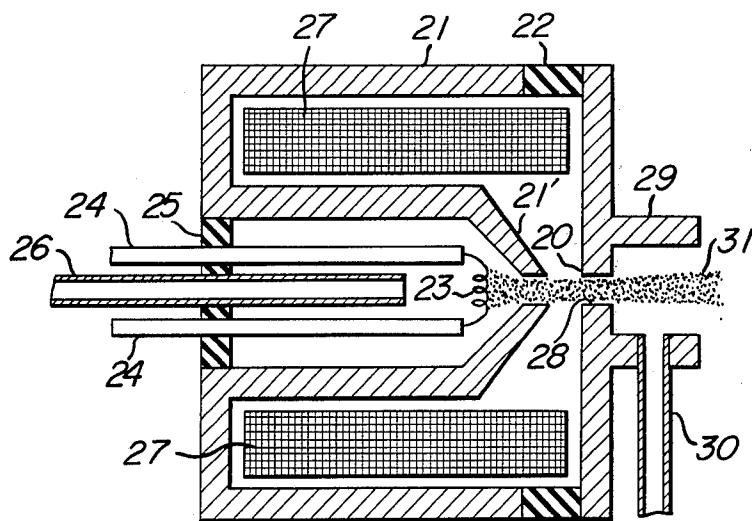




FIG. 9

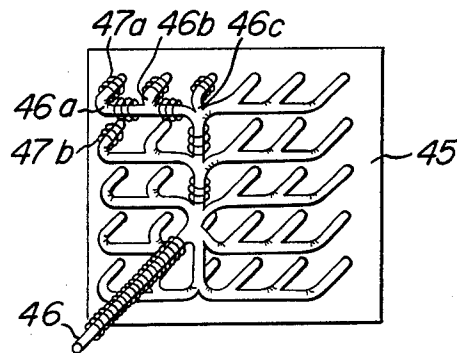


FIG. 10

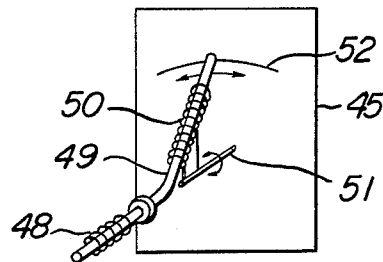


FIG. 11

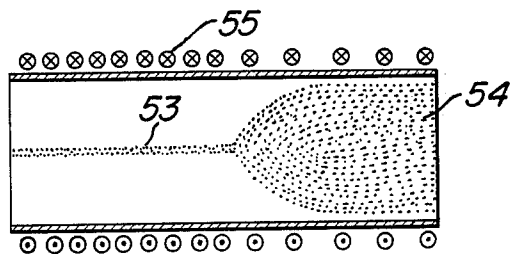


FIG. 12

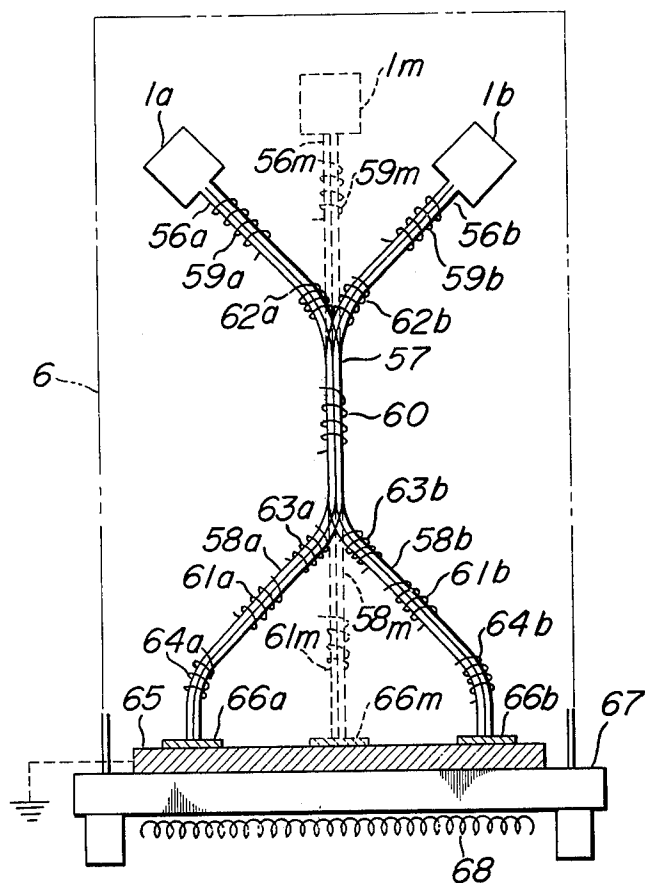


FIG. 13

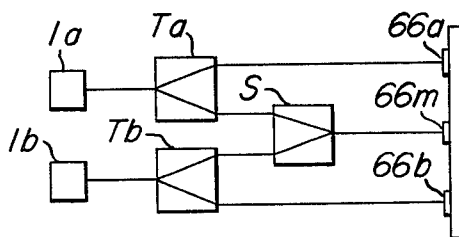


FIG. 14

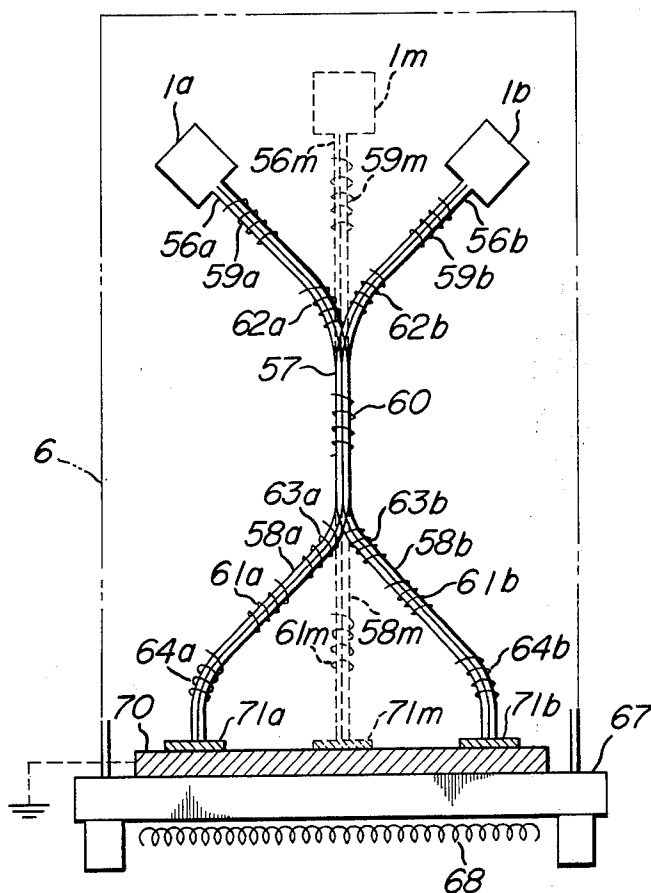


FIG. 15

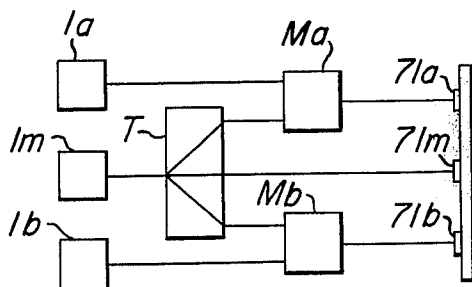


FIG. 16

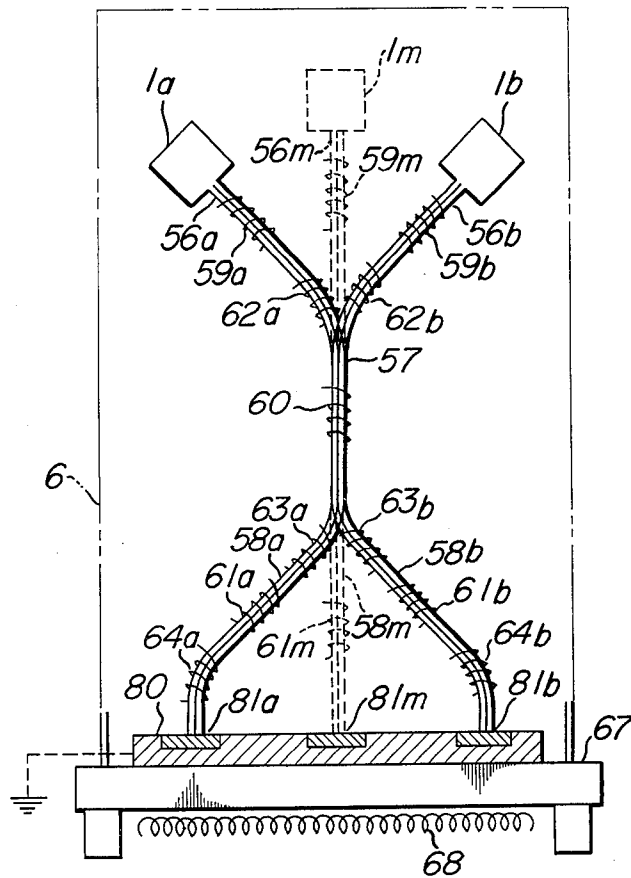
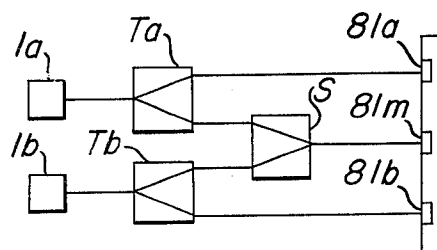


FIG. 17



# METHOD OF TRANSPORTING SUBSTANCES IN A PLASMA STREAM TO AND DEPOSITING IT ON A TARGET

## BACKGROUND OF THE INVENTION

### Field of the Invention

1. The present invention relates to a method and a device for transporting a desired material to a desired object by turning the material into plasma, and more particularly to the improvement of the invention made by the present inventors, disclosed in the specification of Japanese Pat. Publication No. 38801/70 (hereinafter referred to as the "Prior Art").

### Description of the Prior Art

The prior art invention is based in the principle that the stream of plasma composed of ionized gas can be directed to the objective point due to the diffusing effect of the plasma itself and by the control of the plasma stream with axial magnetic fields. The brief explanation of the prior art invention will be described by reference to the attached drawings. In FIG. 1, reference numeral 1 designates a plasma generating section or plasma generator for turning the vapor of a selected material into plasma through electric discharge; 2 a plasma outlet opening of the plasma generator 1; 3 a voltage source for maintaining the plasma generator at a suitable potential; 4 a plasma receiver or collector; 5 an ammeter for measuring electric current carried by a plasma stream 8; 6 the wall of a container to hermetically enclosing the plasma generator 1 and the plasma collector 4, and 7 coils for generating axial magnetic field along the container. The plasma generated in the generator 1 is effused out of the outlet opening 2 due to the difference in density between the plasma inside the generator 1 and that outside the generator 1. The effused plasma is converged by the magnetic field generated by the coils 7 to form a plasma beam 8, which is conducted to the plasma receiver 4 so that the ionized material conveyed in the plasma beam is deposited on the collector 4. The degree of converging the plasma stream and the density of plasma in the stream is changed depending upon the intensity of the axial magnetic field. If the axial field is too weak, the beam of plasma is diverged so that the quality of plasma received by the unit area of the plasma collector 4 is decreased. If the intensity of the axial field is set higher than a certain level (for example, above 200 gauss), the degree of convergence and the density can be kept constant while the plasma is traveling from the generator 1 to the collector 4. Thus, the axial field can be considered to serve as a magnetic pipe for the plasma stream 8. FIG. 2 shows an empirical curve illustrating the relation between the potential V of the plasma applied through the generator 1 by means of the voltage source 3 and the plasma current I measured by the ammeter 5, i.e. current flowing from the plasma stream 8 into the collector 4. If the plasma potential V is lower than the value  $V_e$ , the plasma current I is zero or negative since in this case the plasma stream 8 at the collector 4 the electrons excell in number the positive ions, as seen in FIG. 2. If, on the other hand, the potential V is larger than  $V_e$ , the positive ions excel in number the electrons so that the current I turns positive. As the potential V is increased the current I is increased, and when the potential V reaches the value  $V_s$  the current I saturates at

the value  $I_s$ . Under this condition, no electron reaches the collector 4 due to repelling action and the collector 4 gathers only positive ions.

Therefore, if the plasma current I takes the value  $I_s$  under the application of the plasma potential higher than  $V_s$ , it is considered that the atoms of the material corresponding in amount to the current  $I_s$  by the positive ions are being transported from the generator 1 to the collector 4 in the plasma stream 8. Now, provided that the material to be transported in plasma stream has a valence of 1 when it is turned into plasma in the generator 1, then the weight of the material transported in the plasma stream 8 per unit time: W (gram/sec.) is expressed by the formula

$$W = \frac{I_s(\text{ampere})}{e} \times \frac{M(\text{gram})}{N_o}$$

where M is the atomic weight of the material, e the electric charge of an electron, i.e.  $1.61 \times 10^{-19}$  coulomb, and  $N_o$  Avogadro's number  $6.012 \times 10^{23}$ .

Now, if  $I_s$  is 1 ampere, which is a practical value, and the area of cross section of the plasma stream is  $1 \text{ cm}^2$ , the weight W of the material received by the collector 4 is about 0.29 mg/sec. for silicon and 0.27 mg/sec. for aluminum. In each case, the speed of deposition of the material Si or Al is very high, i.e. about  $1 \mu\text{/sec}$ .

As described above, according to the prior art invention, a selected material can be deposited on a selected object at a great speed, and a predetermined amount of the material can be very accurately transported to a predetermined area of the object. Thus, the accuracy and speed of treatment to the prior art invention is much improved as compared with any conventional method of transporting substances in gas, liquid or solid phase which is used to convey a desired material to a desired place as in vapor-deposition, sputtering, chemical synthesis, semiconductor doping, film formation and crystal growing. Moreover, the method according to the prior art invention is quite different from the substance transporting method using implantation by accelerated ion beam, which came to find its use in a variety of fields. The differences are as follows.

First, the upper limit to the amount of material transported by an ordinary accelerator is  $100 \mu\text{A}$  in terms of ion beam, and even with an isotope separator such a limit is 10 to several 10's of milliamperes. On the other hand, according to the prior art method, it is possible to draw a current of 100 mA to 1A.

Secondly, the conventional implantation method cannot transport the amount of material that is practically needed without immensely increasing the capacity of the overall apparatus to be used. It is, therefore, expensive and far from each operation so that its application to processes is limited. On the other hand, according to the prior art system, there is no need for a high voltage source for acceleration of ionized particles and therefore the apparatus to be used will be small in size and easy of manipulation.

Thirdly, with the conventional implantation method, the energy of, for example, Al ions is about 100 KeV and it is very difficult to obtain an ion beam having a low energy of about 10 to several 10's of eV. In the field of vapor-deposition or semiconductor technology a high energy ion beam cannot be utilized but as ion beam having an energy of about several electron volts is most preferably used. For this reason, the ion beam

is decelerated when the conventional method is used for vapor-deposition or semiconductor technology. In this case, however, the ion beam is diverged in the decelerating process so that the quantity of ions reaching the target is much decreased. Accordingly, it will be hard to obtain a beam having sufficient ions per unit volume. On the other hand, according to the prior art method, the energy necessary to conduct the plasma stream 8 up to the collector is a few volts to several hundred volts in terms of the potential V of the plasma, and in some cases the material can be transported to the collector 4 only due to the diffusion effect, i.e. thermal energy, of the plasma even if the plasma potential V is reduced to zero.

As described above, the method of the prior art invention, i.e. Japanese Pat. Publication No. 38801/70 by the present inventors, is quite different in principle from any conventional method of transporting substance and takes a particular effect when applied for the treatment of semiconductors and the like.

### SUMMARY OF THE INVENTION

One object of the present invention is to provide an improved method of transporting substance in plasma.

Another object of the present invention is to provide an improved method which makes the best use of the merits of transporting substance in plasma stream, in which the kinds and the mixing proportions of the materials transported to a substrate can freely be varied, and in which the shape, area and location of a film made of the transported material can be accurately determined.

An additional object of the present invention is to provide an improved method in which material is turned into plasma and transported to a substrate to form or to grow a single crystal of the material on the substrate.

A further object of the present invention is to provide an improved method in which impurities or semiconductors are transported in plasma stream to semiconductor substrate to fabricate a semiconductor device having p-n junctions or heterojunctions in or on the semiconductor substrate.

Yet another object of the present invention is to provide an improved method of transporting substance in plasma stream.

Briefly state, the subject matter of the present invention will be concentrated as follows. Namely, the vapor of a desired material is turned into plasma by means of a plasma generator, the plasma is effused out of the plasma generator, and the plasma stream is guided by means of axial magnetic field to the surface of a substrate while being converged by the same field. In particular, a plurality of plasma generators are provided to produce plasma streams having different materials, these streams are deflected and mixed together with means for applying magnetic fields which are provided along the streams, and the mixed stream is guided to the substrate to form thereon a layer of compound constituted of the materials.

Accordingly, the device for embodying the method just described comprises a plurality of means for turning a material into plasma and for ejecting the plasma in a fixed direction, means for deflecting the ejected plasma streams, and means for combining the plasma streams, if necessary.

According to the present invention, different materials in plasma state are blended together and the stream of the blended plasma is guided to the substrate to deposit thereon a layer of compound consisting of the different constituents. Moreover, if a crystal which can serve as a seed of single crystal is used as a substrate, the compound deposited on the substrate can be grown as single crystal.

According to the present invention, the simultaneous deposition of different materials on different areas of a substrate is possible.

According to the present invention, a swift transportation of substance to the objective point is possible due to blending a plurality of plasma streams having the same composition.

According to the present invention, a semiconductor is used as substrate, impurities are turned into plasma, the plasma is guided to a predetermined portion of the substrate to deposit thereon the impurities, and the substrate is heated upon or after the deposition of the impurities so as to diffuse the impurities into the semiconductor substrate and to fabricate a semiconductor device.

According to the present invention, a semiconductor in a plasma is deposited on a substrate of a different kind of semiconductor to fabricate a semiconductor device having a heterojunction.

### BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 schematically shows a conventional device for transporting substance in a plasma stream.

FIG. 2 shows an empirical curve representing the potential-current characteristic of plasma.

FIG. 3 is a systematic block diagram of the constitution of a device used to embody the method according to the present invention.

FIG. 4 is a block diagram of a modified equivalent of the main part of the device shown in FIG. 3.

FIGS. 5 to 7 are cross sections of different plasma generators applicable in the device according to the present invention.

FIG. 8 shows in cross section a plasma mixer and it bifurcated portions as an embodiment of the present invention.

FIGS. 9 and 10 are perspective views of different scanners according to the present invention.

FIG. 11 pictorially shows the method of diverging plasma stream, as an embodiment of the present invention.

FIG. 12 is a partially cross-sectional view of a device used to embody the method according to the present invention.

FIG. 13 is a block diagram of a device as another embodiment of the present invention.

FIG. 14 is an illustrative view of a further embodiment of the present invention.

FIG. 15 is a block diagram illustrative of an additional embodiment of the present invention.

FIG. 16 is an illustrative view of a still further embodiment of the present invention.

FIG. 17 is a block diagram illustrative of yet another embodiment of the present invention.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

#### EMBODIMENT 1

FIG. 3 shows schematically the constituents of a de-

vice for transporting substance in a plasma stream according to the present invention. In FIG. 3, as in FIG. 1, numerals 1, 4, 7 and 8 designate plasma generating sections, plasma receiving sections, coils to generate axial magnetic flux for converging plasma stream, and the courses of the plasma streams, respectively. However, in this case, a plurality of plasma generating sections 1, i.e. source of plasma streams, and/or plasma receiving sections 4, i.e. terminals of plasma streams, are provided. There are also shown in FIG. 3 a plasma mixer section S for mixing the plasma streams, a plasma branching section T for splitting a plasma stream into several ones, a neutral particle remover section U, a plasma deflecting means V, indicators E for measuring the density of plasma, and plasma component indicators F. In actual embodiments, only one plasma generating section 1 may be provided to generate a single plasma stream 8 to be conducted to the plasma branching section T while the plasma mixer section S is eliminated, or only one plasma receiving section 4 may be provided to receive the single plasma stream leaving the plasma mixer section S while the plasma branching section T is eliminated. Moreover, according to the present invention, it is possible to propose a constitution, in which, as seen in FIG. 4, a plurality of plasma stream mixers  $S_1, S_2, S_3, \dots$  are provided for groups of plasma streams each of which groups consists of some plasma streams and in which a plurality of plasma stream branchers  $T_4, T_5, T_6, \dots$  each of which receives a single plasma stream and splits it into several streams are provided. Further, in order to provide a more complicated network for plasma transportation, plasma stream mixers  $S_4, S_5, \dots$  to join plasma streams and plasma stream branchers  $T_1, T_2, T_3, \dots$  to branch plasma streams may be inserted in the plasma channels between the plasma stream mixers and branchers  $S_1, S_2, S_3, \dots$  and  $T_4, T_5, T_6, T_7, \dots$ .

The neutral particle remover U may be eliminated depending upon application.

Of the above described constituents of the device for transporting substance in plasma stream, the embodiments of plasma generating section 1 will first be described. FIG. 5 shows an embodiment of a low-voltage arc type plasma generator, in which a plasma source container 9 serving also as an anode for arc discharge is made of heat resistive electric conductor such as stainless steel or carbon. A substance 14 to be transported, contained in the vessel 9 is thermally evaporated by means of a heating section 10 consisting of a heater 12 insulated with non-conductive materials 11 and 13 and the vapor pressure within the container 9 is kept at about  $10^{-2}$  Torr or less at which discharge can take place properly. A filament 16 serving as a cathode electrode for discharge is made of tungsten or tantalum wire having a diameter of, for example, 1 mm, and mounted on a pair of supporting rods 15 made of conductive metal, piercing the wall of the container 9 maintaining hermetical seal with the wall and insulated from the wall. The filament in operation is made to glow by the supply of a current of 100 A with a voltage of 3 V supplied across it. If under this condition a d.c. voltage of about 200 – 300 V is applied between the cathode filament 16 and the wall of the container 9 as the anode, low-voltage arc discharge takes place at a vapor pressure of about  $10^{-2}$  Torr to allow arc current of 1 – 3 A to flow. Since, in this case, the container 9 is placed in the axial magnetic field, indicated by arrow

B, produced by means of the coil 7 and since the filament 16 as cathode is provided near a plasma outlet opening 17 cut in the wall of the container 9 which serves as anode, the established low-voltage arc discharge is concentrated near the space between the filament 16 and the plasma outlet opening 17 to turn the vapor of material to be transported into high density plasma. The high density plasma is then effused out from the container 9 through the opening 17 into the outer atmosphere due to the difference in density between inside and outside of the opening 17. And the axial field is present in a predetermined direction due to the coil 7 so that the plasma stream 19 flowing out of the outlet opening 17 through diffusion effect is converged into a small-diameter beam and continues to diffuse along the direction of the axial magnetic field. The axial magnetic field can be considered to serve as a sort of pipe for conducting plasma stream there-through because it enables plasma stream to flow through space while preventing the diameter of the stream from increasing. Hence, the course of plasma stream guided by the axial field may hereafter be referred to as a "magnetic pipe" or "magnetic channel".

If a material to be transported is a gas or a liquid having a high vapor pressure at room temperatures, it can be introduced into the container 9 through a pipe 18 as shown in FIG. 5. The quantity of the fluid flow is controlled by an appropriate needle valve so that the vapor pressure of the material may stand appropriate to arc discharge. In case where a material to be transported has too high a melting point to obtain a vapor pressure appropriate to arc discharge due to an ordinary glow heating, it is necessary to introduce inert gas such as helium or argon as discharge carrier through the pipe 18. As a result, the obtained plasma consists of a mixture of a large part of ions of the carrier gas and a small port of ions of the material to be transported.

FIG. 6 shows another embodiment of the invention, i.e. a plasma generating section of duoplasmatron type. In FIG. 6, numeral 20 indicates an anode and numeral 21 designates a double cylinder having an inner cylinder whose free end serves as an intermediate electrode 21' and an outer cylinder which serves as a plasma container, and accommodating a coil 27 to generate an axial magnetic field in the space between the inner and outer cylinder. The anode 20 and the double cylinder body 21 are both made of electrically conductive ferromagnetic material such as iron or the like. The magnetic flux induced by the coil 27 is closed through a circuit comprising the anode 20, an insulating piece 22, the intermediate electrode 21' and the air gap between the electrode 21' and the anode. A pair of lead wires 24 and a pipe 26 are inserted into the inner cylinder of the double cylinder body 21 is insulated and hermetical condition by means of an insulating pad 25. A filament 23 is mounted on the pair of lead wires 24, and is powered through the wires 24. The pipe 26 serves to introduce the gas or vapor of material to be transported or carrier gas such as helium, argon or the like, if necessary. Numeral 28 designates a plasma outlet opening cut in the anode 20. Now, the material in gaseous or vapor state to be transported is conducted through the pipe 26 into the inner cylinder and the gas pressure in the inner cylinder is controlled so as to be kept at about  $10^{-2}$  Torr, the filament 23 is energized, and voltages of about 200 V and about 80 V are applied respectively between the filament 23 and the anode 20 and between

the filament 23 and the intermediate electrode 21'. Then, a low-voltage arc discharge takes place so that a discharge current of about 3A flows, the major portion of the current flowing between the filament 23 and the anode 20 and the minor portion between the filament 23 and the electrode 21'. The arc established due to the discharge has its diameter limited by the inner diameter of the free end of the inner cylinder, i.e. intermediate electrode 21', and moreover is focussed by the axial magnetic field having a high flux density as a result of being concentrated in a narrow gap between the free end of the inner cylinder and the anode so that high density plasma is produced in the discharge path between the intermediate electrode 21' and the anode 20. The thus produced plasma effuses out from the outlet opening 28, as described with FIG. 5. In this way, a high density plasma stream can be obtained, but the plasma generator of this type has a rather complicated constitution so that the utility factor of the vapor turned into plasma is largely lowered since part of the vapor of materials to be transported deposits on the wall of the container. Further, in case where chemically active gas such as oxygen or chlorine is introduced into the container, the cathode filament 23 will be rapidly eroded so that its operative life is shortened. In order to eliminate such drawbacks as mentioned above, inert gas such as helium or argon is introduced into the container through the pipe 26 to cause low-voltage discharge to take place, while a pipe 29 having a diameter larger than that of the outlet opening 28 is connected to the outer surface of the anode 20, as seen in FIG. 6, into which gas or vapor of the material to be transported is conducted through a smaller pipe 30. The plasma generated near and inside the outlet 28 is jetted into the pipe 29 due to the difference in density. Since there are in the jetted plasma a vast number of ions of inert gas such as helium, for example, and of electrons given discharge energy, the gas or vapor introduced through the pipe 30 into the pipe 29 is ionized partially by the ions of the inert gas due to charge exchange therebetween and mostly by the electrons in the plasma. Thus, a high density plasma 31 of the material to be transported is produced in the pipe 29. The mechanism of the high density plasma being conveyed along the axial magnetic field while being focussed by the field is the same as that described with FIG. 1 and FIG. 5.

Fig. 7 shows a plasma generator of high frequency discharge type in which discharge is established under the influence of high frequency electric field. For example, the gas or vapor of material to be transported is fed through a pipe 33 into a discharge tube 32 which is made of insulating material such as glass or quartz and the gas pressure inside the tube 32 is maintained at about  $10^{-2}$  Torr. And if a high frequency voltage of 20 to 100 MHz is applied between a pair of ring electrodes 34 provided on the tube 32 in appropriately spaced relation to each other, the gas of the material to be transported is turned into plasma due to the electrodeless discharge taking place in the discharge tube 32, so that plasma 36 streams out of the outlet opening 35. If it is desired to maintain the potential of the plasma stream 36 at a predetermined level, it is only necessary to connect with an appropriate voltage source a probe electrode 37 inserted in the tube 32. It should also be noted that the condenser coupling method of application of

a high frequency voltage may be replaced by an induction coupling method.

The conventional ion source used for, for example, the conventional accelerator or mass analyser has in principle the same constitution as that used for the plasma generators described above and therefore it can be used as a plasma source in the present invention if it is slightly modified according to its purpose.

Reference should now be made to FIG. 8 in which is shown a plasma mixer section S, or  $S_1$  to  $S_8$ , as shown in FIGS. 3 and 4, which mixes a plurality of plasma streams with one another. In this figure, reference numerals 38a and 38b respectively designate evacuated pipes leaving plasma generators 1a and 1b; 39a and 39b flexed portions of the evacuated pipes 38a and 38b, respectively; 40 a confluence pipe at which the pipes 38a and 38b join together; 41a and 41b coils for generating axial magnetic field respectively, in the pipes 38a and 38b; 42a and 42b deflecting coils for generating axial magnetic field along the flexed portions 39a and 39b; and 43a and 43b coils for generating axial magnetic field in the confluent pipe 40. The coils 43a and 43b are shown in FIG. 8 as separately provided, however, they may be formed in a single unit.

The coils 41a, 42a and 43a generate continuous axial magnetic field along the flexed channel from the pipe 38a to the confluence pipe 40 and thereby conduct the plasma stream 44a leaving the generator 1a to the confluence pipe 40 while focussing the plasma stream 44a in the center of the flexed channel. Similarly, the coils 41b, 42b and 43b generate continuous axial magnetic field along the flexed channel from the pipe 38b to the confluence pipe 40 and thereby conduct the plasma stream 44b leaving the generator 1b to the confluence pipe 40 while focussing the plasma stream 44b in the center of the flexed channel. The plasma streams 44a and 44b join together in the confluence pipe 40. In this way, the different materials to be transported, included in the separate plasma streams are mixed together at the point S of confluence and thereafter the mixed plasma, i.e. mixed materials to be transported, is further conveyed. The just described constitution of the plasma mixer section is for the case where only two plasma generators are employed. And also in case where three plasma streams join together, as in FIG. 4, or where a plurality of plasma streams are mixed together, as in FIG. 3, the plasma mixer section to be used for this purpose is not different from that used to two plasma streams except that the number of evacuated pipes having flexed portions together with the number of associated coils for generating axial magnetic flux therein is increased. It should be noted that when the mixer section shown in FIG. 8 is used as the mixer section  $S_4$  or  $S_5$  shown in FIG. 4, the generators 1a and 1b shown in FIG. 8 are to be substituted by the devices  $T_1$  and  $T_2$  or  $T_2$  and  $T_3$ . Further, one of the plurality of plasma streams may be left non-deflected while the other plasma streams are deflected. Switches (not shown) may be used in the exciting circuit of the coils so as to conduct any desired plasma stream to advanced stages or to block only a desired one of several plasma streams so that it may not join the other.

The merits of deflecting a plurality of plasma streams to make them join one another, which considerably add to the utility of the method of transporting substance in the plasma streams, are counted as follows.

1. A great quantity of plasma can be transported by the use of a plurality of plasma generators each having a small capacity, without employing any plasma generator having a large capacitor which cannot be easily fabricated or incorporated.

2. A plurality of materials which cannot coexist in a single plasma generator can be separately turned into the corresponding plasmas and thereafter be joined together.

3. Any desired material can be rapidly transported to its objective points by switching over the axial magnetic field. And a variety of materials can in turn be transported to one and the same objective point. This is very important when a plurality of materials have to be transported which cannot be mixed during transportation in plasma stream because of their chemical reactivity to one another.

4. The ratio of the material transported by the plasma stream 44a to the object to the material transported by the plasma stream 44b to the same object can be arbitrarily controlled by controlling the ratio of the repetition period of excitation of the coils 41a to that of the coils 41b.

Now, in order to give descriptions of plasma branching section T or  $T_1$  to  $T_7$  as shown in FIGS. 3 and 4, some modifications and alteration should be made to FIG. 8. Namely, let the reference character S be substituted by T; let the direction of the arrow indicating the flow of plasma 44 be inverted; and let the plasma generators 1a and 1b be substituted by plasma receiving sections 4 as shown in FIG. 3. And the function of the plasma branching section T is explained by reference to the thus modified FIG. 8. (The plasma stream 44 now transported from the right through the confluence pipe 40 by means of the combined effect of axial magnetic fields generated by coils 43a and 43b is branched at the diverging point into two plasma streams 44a and 44b due to the branching components of the axial fields generated by deflecting coils 42a and 42b). Moreover, it is clear that more than two plasma streams can be derived on the principle of branching and that the control of the plasma streams 44a and 44b can be effected by controlling the exciting currents for the coils 41a, 42a and 41b, 42b since the plasma branching section has a function inverse to that of the plasma mixer section. The merits of branching a single plasma stream into several ones with such a plasma branching section as described above, are as follows.

1. The simultaneous transportation of material from a single plasma source to a plurality of tiny objects or objective points is possible.

2. The switching-over of material transportation to different objects or objective points can be done by switching over the axial fields. For example, with a structure as shown in FIG. 9, the main plasma stream 46 is branched out into a plurality of plasma streams 46a, 46b, 46c, . . . directed to the different points on the object 45, and by sequentially switching over the axial magnetic fields generated by means of coils 47a, 47b, . . . etc. for the plasma streams 46a, 46b, . . . , etc. the object is reached by the plasma streams 46a, 46b, . . . , etc. sequentially in this order so that the object 45 can be scanned by the plasma streams. Further, if a flexed pipe 49 is connected with the pipe 48 for main plasma stream in rotatable and hermetical condition, as seen in FIG. 10, with a coil 50 generating axial magnetic field wound about the flexed pipe 49, then the surface of the

object can be continuously scanned by the plasma stream when the rotatably connected flexed pipe 49 is rotated about the axis 51 perpendicular to the surface of the object 45. In this case, the scanning follows a fixed locus. This way of canning is not one under consideration, but the combination of the branching structure as shown in FIG. 9 and the rotating structure as shown in FIG. 10 may simplify to a certain extent the overall constitution.

According to these scanning methods, a rapid and exact transportation of material to a plurality of objective points and to a specific region on the object having a predetermined pattern can be performed. In addition, these methods are meritorious also in that a single plasma stream having a predetermined density can be diverged or converged to obtain a plasma stream having a larger or smaller diameter but the same density.

The practical artifice to diverge the plasma stream is shown in FIG. 11. Namely, the distance between the adjacent turns of the coil 55 is changed at a point and the changed distance is maintained until another change or restoration is needed. The coil 55 is wound thicker before the point and more spaced after the point so that the plasma stream 53 is diverged at that point to be a thinner one 54, i.e. the density of the latter being smaller than that of the former. This is not a technique of branching a plasma stream, which the present invention intends to provide, but is a means to be effectively used in the method according to the present invention. This means can also be used to converge plasma stream if the direction of the stream is reversed. In this case, the density of the plasma stream after convergence is the same as that of the plasma stream before convergence since these plasma streams are both diffused ones.

3. By constituting the device as shown in FIG. 4 with the branching and combined structures described above, a great number of plasma streams having different components and compositions can be obtained from rather less plasma sources each having a single substance.

As described above, the utility of the prior art device for transporting substance in plasma stream as shown in FIG. 1 will be improved if the mixing of plasma streams and/or the branching of a plasma stream is performed by providing magnetic deflecting means in the conducting pipes for plasma streams and/or the branching of a plasma stream is performed by providing magnetic deflecting means in the conducting pipes for plasma streams of the device.

Now, the explanation will be made of an improved method of transporting substance in plasma streams, as one embodiment of the present invention, used to form thin films. Reference should be had to FIG. 12 for the help of understanding. In the figure, reference characters 1a, 1b and 1m designate different plasma generating chambers; 56a, 56b and 56m pipes for conducting the flows of the generated plasma therethrough; 57 a confluence plasma pipe for joined plasma streams; 58a, 58b and 58m pipes for branched plasma streams; 59a, 59b and 59m axial coils for the pipes 56a, 56b and 56m; 60 axial coils for the confluence pipe 57; 61a, 61b and 61m axial coils for the pipes 58a, 58b and 58m; and 62a and 62b, 63a and 63b, and 64a and 64b axial coils for deflecting plasma streams, each of the coils 62a to 64a and 62b to 64b being partially shown. Numeral 65 indicates a substrate on the surface of which thin film 66a,

66b and 66m is to be formed, and 67 a supporting platform on which the substrate 65 is rested. All the articles on the supporting platform 67 are kept in vacuum by means of an enclosing wall of a container 6.

In case of forming blended film of Zn and Mg on the substrate 65 of iron, Zn vapor and Mg vapor are turned into plasma in the plasma generating chamber 1a and 1b, respectively. The thus obtained Zn plasma stream in the pipe 56a and Mg plasma stream in the pipe 56b join together by means of the deflecting coils 62a and 62b to form a blended plasma stream consisting of Mg and Zn plasma in the confluence pipe 57. Then, the blended plasma stream is branched out into two plasma streams to be conducted through the pipes 58a and 58b or three plasma streams to be conducted through the pipes 58a, 58b and 58m by means of the deflecting coils 63a, 63b and 63m. The branched blended plasma streams are directed to the substrate 65 through deflection by means of the deflecting coils 64a and 64b so that Zn and Mg ions transported in the blended plasma streams are deposited on the surface of the substrate 65 to form thin films 66a 66b or 66a, 66b and 66m. If, for example, it is desired to form only a thin film 66m, it is only necessary to deenergize the coils 61a and 61b for the branched pipe 58a 58b and the deflecting coils 63a, 63b and 64a, 64b but to energize the coils 61m alone. It is clear that in order to form thin films 66a 66b only the coils associated with the branched pipe 58a 58b have to be energized. Also, in case where a plurality of thin films of a single substance, for example, of Zn are formed on the substrate 65, only the plasma generator 1m is used to generate Zn plasma stream, and after the Zn plasma stream has been led into the confluence pipe 57, it is branched out in the same manner as described above.

Further, in order to have thin films 66a, 66b and 66m respectively of Zn alone, Mg alone and the blend of Zn and Mg, only the 59a, 62a, 60, 63a, 61a and 64a associated with the pipes 56a, 57, and 58a conducting the Zn plasma stream from the plasma generator 1a to the film 66a are energized to form the film 66a of Zn, then in like manner only the coils associated with the pipes conducting the Mg plasma stream from the plasma generator 1b to the objective point 66b are energized to form the film 66b of Zn, and finally the coils 59a, 62a and 59b, 62b respectively for the Zn plasma stream and the Mg plasma stream and the coils 60 and 61m respectively for the confluence pipe 57 and the pipe 58m are energized to form the blended film 66m of Zn and Mg. With this device shown in FIG. 12, however, it is impossible to simultaneously form the thin film 66a, 66b and 66m. If it is required to form the three film at a time, another structure has to be employed which is shown in FIG. 13 as a block diagram resembling that shown in FIG. 4. Namely, Zn plasma stream from a plasma generator 1a is brached into two Zn plasma streams by means of a plasma stream brancher Ta, while Mg plasma stream from a plasma generator 1b is branched into two Mg plasma streams by means of a plasma stream brancher Tb. One of the two Zn plasma streams is directed to the substrate to form thereon a Zn film 66a, and similarly one of the two Mg plasma streams is directed to the substrate to form thereon a Mg film 66b. The remaining one of the Zn plasma streams and the remaining one of the Mg plasma streams join together by means of a plasma stream mixer S and the blended plasma of Zn and Mg is directed to the substrate to

form thereon a blended film of Zn and Mg. Thus, the three thin films can be formed simultaneously.

The method according to the present invention is especially useful for the formation of thin films in semiconductor devices. As one of preferred embodiments of the method, the formation of SiO<sub>2</sub> film on Si substrate is explained. Plasmas of Si, O<sub>2</sub> and Al are generated by the plasma generators 1a, 1b and 1m. The Si plasma stream through the pipe 56a and the O plasma stream through the pipe 56b join together in the confluence pipe 60 to form a blended plasma stream, which reaches the surface of the Si substrate 65 through at least one of the branched pipes 58a, 58b and 58m to form thereon SiO<sub>2</sub> film. Then, the generation and transportation of the Si and O plasmas is ceased and, in turn, Al plasma is generated by the plasma generator 1m. The Al plasma stream is conducted through the pipe 56m and the confluence pipe 60 up to the point of branching and it is diverted to the pipe through which the blended plasma stream was guided. The Al plasma stream, passing through the selected pipe, reaches the previously formed SiO<sub>2</sub> film and formed thereon an Al film. Thus, the formation of the SiO<sub>2</sub> insulating film and the Al conducting film for wiring can be easily and quickly performed on the Si substrate by merely switching over the energization of axial coils for plasma stream conducting pipes. Also, multi-layer circuit or wiring structure can easily be fabricated by repeating the above described processes. If boron B or phosphorus P is added to the SiO<sub>2</sub> through simultaneous transportation of plasma, the so called doped oxide film can be resulted in.

in addition to the application to the semiconductor devices, the method according to the present invention finds its use in the formation of metal multiple layer such as Au-Mo multiple layer constituted of alternate Au and Mo layers. It will be needless to say that in this case the coils for the Au and Mo plasma streams should be alternately energized. Moreover, if a blended plasma stream consisting of two or more kinds of metals is directed to the substrate 65 which is heated, as seen in FIG. 12, up to temperatures above 300°C by means of an appropriate heating means 68, then a thin alloy film is formed in the surface of the substrate 65.

Further, a thin film of chemical product such as oxide or halogenide can be formed on the substrate by combining or switching over the magnetic fields for the paths of plasmas of metal or other inorganic substances and those for the paths of plasmas of halogenides or oxides. Examples of such compound films are, besides SiO<sub>2</sub> film from Si and O<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> from Al and O<sub>2</sub> and MoCl<sub>3</sub> from Mo and Cl. If the substrate 65 is heated above 300°C, as described above, the chemical reaction during the formation of such compound films will be promoted.

Still further, the superposed formation of different layers having different compositions such as Al<sub>2</sub>O<sub>3</sub> and Si<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> can be performed according to the present invention.

According to the method of present invention, the diameter of the plasma beam is as small as 3 to 4 mm due to the convergence effect of the axial magnetic field, the substrate it is sometimes preferable to increase the diameter of the plasma beam by diverging the plasma beam according to the technique described with FIG. 11. A mask having perforations in a predetermined shape or a slit is placed in front of the target sub-

strate so that a thin film having the predetermined shape is formed on the substrate, as in the masking method used in the conventional semiconductor technology.

As has hitherto been described, the method according to the present invention is characterized in that a great number of different thin films can easily be produced and that the compositions of the different thin films can freely be varied. And this feature will be added to the merit of forming a thin film according to the method of transporting substance in plasma stream. Each of particles constituting plasma stream is an ion having a certain electric charge. Therefore, there appears the concentration center of an infinite number of the ionized particles on the surface of deposit of the substrate so that uniform and firm deposit becomes possible.

This advantageous feature is now combined with that according to the present invention.

Provided that, as described with FIG. 1, a power source 3 is connected with the plasma generator 1 to maintain the plasma stream at a potential of, for example,  $V_0$  and that the receiver 4 or the substrate 65 in FIG. 12 is grounded, each particle of the plasma stream is implanted in the substrate 65 at an energy of  $eV_0$  (i.e. 100 eV when  $V_0$  is 100 V) to adhere very firmly to the same. If, on the other hand, Ar plasma is transported to an Si substrate at an energy of 300 eV, sputtering onto the surface of the Si substrate takes place due to the energized argon atoms. So, if this sputtering is performed on the substrate before the formation of any desired film, the surface of the substrate on which a thin film is formed is cleaned. And this will assure the firm adhesion of the resultant thin film to the substrate. In addition to the effect of cleaning the surface of the substrate, this sputtering method can also be used to perforate the  $SiO_2$  layer. For this sputtering method, different from sputtering by ion beam, can effectively applied to such an insulating material as  $SiO_2$ . For example, by depositing a film of conducting material such as Al on the  $SiO_2$  film after the perforating operation is formed a wiring layer.

## EMBODIMENT 2

Another embodiment of the present invention will be described which is applied to a case where the crystal of a material is grown. For better understanding the embodiment reference should be had to FIG. 9. In FIG. 14, the same reference numerals as in FIG. 12 have been applied to like constituents and the explanation of the parts mentioned with FIG. 12 is omitted here. Numeral 70 indicates a substrate crystal and crystals are grown at the portions 71a, 71b and 71m of the substrate crystal 70.

As a first example, crystal of GaAs is epitaxially grown on the substrate 70 made of a single crystal of GaAs. First, the vapors of Ga and As are turned into plasmas respectively in the plasma generator 1a and 1b and the thus obtained Ga and As plasma streams conducted respectively through the pipes 56a and 56b are made to join together by means of the deflecting coils 62a and 62b to produce a blended plasma stream of Ga and As in the confluence pipe 57. The blended plasma stream is then branched into two or three streams conducted through the pipes 58a and 58b or the pipes 58a, 58b and 58m by means of the deflecting coils 63a and 63b, and thereafter the branched plasma streams

through deflection by the coils 64a and 64b and the plasma stream not deflected are directed perpendicularly to the surface of the substrate 70 so that Ga and As ions present mixed in the plasma streams coheres to the surface of the substrate 70 made of a single crystal of GaAs to grow crystals of GaAs at the positions 71a, 71b and 71m. Now, if only the crystal 71m is desired to be grown, it is only necessary to energize the axial coils 61m alone, but not to energize the axial coils 61a and 61b for the pipes 58a and 58b and the deflecting coils 63a, and 64a and 63b 64 b. It will therefore be clear that if only the crystals 71a and 71b are desired to be grown it is only necessary to energize the coils associated with the pipes 58a and 58b. As a second example, a single substance such as, for example Si is grown at a plurality of portions of the surface of an Si single crystal 70. In this case, only the plasma generator 1m is used to produce an Si plasma stream in the pipe 56m. The Si plasma stream, after passing through the confluence pipe 57, is branched out as described above. With the coils 61m energized, the Si plasma stream makes its straight way toward the substrate 70 to grow Si crystal thereon. As a third example, an Si intrinsic semiconductor crystal, a P-type silicon semiconductor crystal and an N-type silicon semiconductor crystal are grown respectively at the positions 71m, 71a and 71b on an intrinsic semiconductor substrate 70 of silicon single crystal. In this case, Si plasma is generated in the chamber 1m and diffused into the pipe 56m to form a stream of Si plasma while the plasmas of a P-type impurity such as  $I_n$  and an N-type impurity such as Sb are generated respectively in the plasma generating chambers 1a and 1b and diffused into the pipes 56a and 56b to form streams of plasmas of  $I_n$  and Sb. First, the Si plasma stream is guided to the place 71m on the substrate 70 by means of the axial coils 59m, 60 and 61m so as to form in the place 71m an epitaxially grown crystal of intrinsic silicon semiconductor. Then, only the  $I_n$  plasma stream is guided to the confluence pipe 57 by blocking the Sb plasma stream by deenergizing the axial coils 59b for the pipe 56b but advancing the  $I_n$  plasma stream by energizing the axial coils 59a for the pipe 56b. The  $I_n$  plasma streams and the Si plasma stream join together in the confluence pipe 57. The blended plasma stream is further advanced through the pipe 57 by the energization of the axial coils 60 until it reaches the branching point. If the coils 61m, 63b, 61b and 64b are deenergized and if the coils 63a, 61a and 64a are energized, the blended plasma of Si and  $I_n$  reaches the place 6a on the substrate 65 to form thereon an epitaxially grown P-type layer. In like manner, if only the  $I_n$  plasma stream is blocked by deenergizing the axial coils for the pipe 56a, the Sb plasma stream is guided into the confluence pipe 57 and therein blended with the Si plasma streams. Now, if only the coils 63b, 61b and 64b associated with the branched pipe 58b are energized, the blended plasma stream hits the portion 71b of the substrate 65 so that an N-type layer is epitaxially grown. Thus, the three kinds of grown layers which were desired to be formed can be resulted in by the above described procedure. With this constitution as shown in FIG. 14, however, the simultaneous formation of these three layers are impossible. In order to make possible such a simultaneous transformation, a system should be employed which is shown in block representation in FIG. 15. Namely, the Si plasma stream from the plasma generator 1m is split by

means of a plasma brancher T into three streams, one of which is directed to the place 71m, another of which joins the  $I_n$  plasma stream from the generator 1a in the mixer Ma so that the blended plasma stream is directed to the place 71a, and the rest of which joins the Sb plasma stream from the generator 1b in the mixer Mb so that the blended plasma stream is directed to the place 71b. Therefore, the desired three kinds of layers can simultaneously be formed as desired. Further, if branched channels leading to the place 71a, 71b and 71m are provided for each of the blended plasma streams from the mixers Ma and Mb and if those channels are appropriately switched over by suitably energizing and deenergizing the axial coils associated with the channels, then the stream of the blended plasmas of Si and  $I_n$  and that of the blended plasmas of Si and Sb can be selectively directed to any one of the places 71a, 71b and 71m, e.g. place 71a, so that a P-N or N-P double-junction layer or a multi-junction layer having P-N-P-N-P . . . or N-P-N-P . . . structure can be grown through epitaxial crystallization. Moreover, if the mixing proportion of the blended plasma consisting of Si and  $I_n$  to that consisting of Si and Sb is controlled, a multilayer consisting of crystal grown layers having different doping quantity such as P<sup>+</sup>P, PP<sup>+</sup>, n<sup>+</sup>n or nn<sup>+</sup> layers can be formed.

In sum, it is concluded that a variety of crystal grown layers can be obtained; the location, shape and area of the grown layers being freely and accurately chosen, by the use of the suitable combination of the plasma stream mixing, branching and diverging methods described with FIGS. 3 and 4.

It is often necessary to heat the substrate crystal up to appropriate temperatures with a heater 68 as shown in FIG. 14 while the crystal is grown by plasma stream. Even in case where the substrate is heated, however, the temperatures at which Si crystal is grown are rather low, i.e. about 500°C, so that no diffusion of impurity takes place in or near the junctions between superposed different layers as of such a multilayer as described above. Accordingly, abrupt step junctions can be obtained. This is one of considerable merits in fabricating semiconductor device.

According to the method embodying the present invention, the formation of a heterojunction in semiconductor devices becomes possible. One example of forming a heterojunction will be described by reference to FIG. 14. Germanium Ge is used as the substrate 70, and Ga and As are turned into plasma in the plasma generator 1a and 1b, respectively. These plasmas of Ga and As are conveyed to a predetermined place on the germanium substrate to grow thereon a GaAs crystal.

According to the method of the present invention, the diameter of the plasma beam is as small as 3 to 4 mm due to the convergence effect of the axial magnetic field, and in order to form a thin film on a larger area of the substrate it is sometimes preferable to increase the diameter of the plasma beam by diverging the plasma beam according to the technique described with FIG. 11. A mask having perforations in a predetermined shape or a slit is placed in front of or on the target substrate so that an epitaxial crystal having the predetermined shape is grown on the substrate, as in the masking method used in the conventional semiconductor technology.

As has been described, the method according to the present invention is characterized in that a great num-

ber of different crystals can easily be grown and that the compositions of the different grown crystals can freely be varied. And this feature will be added to the merits of growing a crystal according to the method of transporting substance in plasma stream. Further, provided that, as described with FIG. 1, a power source 3 is connected with the plasma generator 1 to maintain the plasma stream at a potential of, for example,  $V_0$  and that the receiver 4 or the substrate 70 in FIG. 14 is grounded, each particle of the plasma stream at the surface of the substrate 70 has an energy of  $eV_0$  (i.e. 50 eV when  $V_0$  is 50 V) so that even if the temperature of the substrate 70 is low the crystal can be grown due to the part of energy absorbed in the substrate.

If the Si plasma is transported to the substrate of Si crystal at an energy smaller than the association energy of silicon atoms, i.e. 10 eV, the whole energy 10 eV is distributed as thermal energy to the particles of the Si plasma arrived at the substrate without causing sputtering and defects on the substrate itself so that the crystal can be grown without flaw and defect even in case where the temperature of the substrate is rather low. This is true for the process of growing the crystal of compound semiconductor.

If, on the other hand, Ar plasma is transported to Si substrate at an energy of 300 eV, sputtering onto the surface of the substrate of Si crystal takes place due to the energized argon atoms. So, if this sputtering is performed on the substrate prior to the growing of a desired crystal, the surface of the substrate is cleaned and becomes free of contaminations so that the crystal can be grown in a preferable condition.

### EXAMPLE 3

This is a process of doping a semiconductor substrate with impurities according to the method of present invention in which substance is transported in plasma stream. For the better understanding of the embodiment reference should be had to FIG. 16. In FIG. 16 the same reference numerals as in FIG. 12 have been applied to like constituents and the explanation thereof is not repeated here, though newly introduced parts are not the case. A substrate 80 is shown as having three portions 81a, 81b and 81m doped with impurities.

For example, in case of simultaneously doping a substrate 80 of silicon single crystal with As and B having different diffusion coefficients, the vapors of arsenic As and boron B are first turned into plasma respectively in the plasma generator 1a and 1b so that the As and B plasma streams produced in the pipe 56a and 56b are forward conveyed by means of the coils 59a and 59b and join each other, by means of the coils 62a and 62b, in the confluence pipe 57 to produce a stream of blended plasma consisting of As and B therein. Then, the blended plasma stream is branched into three streams by means of the deflecting coils 63a and 63b or two streams by means of the same deflecting coils and the coil 61m. The plasma stream in the pipe 58m is directed by means of the coil 61m perpendicularly to the surface of the portion 81m of the substrate 80 while the plasma streams in the pipes 58a and 58b are directed perpendicularly to the surfaces of the portions 81a and 81b of the substrate 65 by means of the deflecting coils 64a and 64b, respectively. Therefore, the ions of As and B conveyed in the blended plasma streams stick to and become deposited on the surfaces of the portion 81a, 81b or 81m. Now, if the substrate is heated up to

temperatures of 1000–1200°C by means of a suitable heating device such as shown indicated at 68 in FIG. 16, the As and B atoms will be diffused into the Si substrate 65 according to their diffusion coefficients. Since the diffusion coefficient of B is greater than that of As, two n-p-n junction layers in superposition can be obtained if the Si substrate is of n-type. If, on the other hand, the blended plasma stream is contacted with the substrate 80 while the latter is heated at 1000° to 1200°C, both the impurities As and B are diffused into the substrate 80 as soon as they have come in contact therewith so that doping along with diffusion process becomes possible. Moreover, if the supporting platform 67 is shifted horizontally, it is also possible to successively dope with impurities a plurality of substrates 80 placed on the platform 67. If only the portion 81m is desired to be doped with impurities, it is only necessary to energize the coils 61m alone with the coils 61a and 61b for the branched pipe 58a and 58b and the deflecting coils 63a, 63b and 64a, 64b deenergized. It is, therefore, clear that if only the portion 81a or 81b is desired to be doped only the coils associated with pipe 58a 58b needs to be energized with the coil 61m deenergized. If only a substance, for example, As is desired to be deposited on a plurality of portions of the substrate 80, only the plasma 1m is used to produce As plasma stream in the pipe 56m. The As plasma stream is guided into the confluence pipe 57 and thereafter branched out as described above.

Now, if the portions 81a, 81b and 81m of the substrate 80 need to be doped respectively with As, B and both of As and B, the following procedure should be carried on. Namely, the plasma generator 1a is first operated to produce As plasma stream in the pipe 56a and at the same time only the coils 59a, 62a, 60, 63a, 61a and 64a associated with the pipes 56a, 57 and 58a are energized so that only the portion 81a is doped with As atoms. Then, the plasma generator 1b is operated to produce B plasma stream in the pipe 56b and at the same time only the coils 59b, 62b, 60, 63b, 61b and 64b associated with the pipes 56b, 57 and 58b are energized so that only the portion 81b is doped with B atoms. And finally, both the plasma generators 1a and 1b are operated to produce As and B plasma streams respectively in the pipe 56a and 56b and simultaneously only the coils 56a and 56b, 62a and 62b, 60 and 61m are energized so that the blended plasma is transported to the portion 81m, resulting in doping the portion 81m with both As and B atoms. With the device having such a constitution as shown in FIG. 16, however, it is impossible to simultaneously dope the portions 81a, 81b and 81m with impurities. In order to make possible such a simultaneous doping, a system should be employed which is shown in block representation in FIG. 17. Namely, the As plasma stream from the generator 1a is split by means of a plasma brancher Ta into two streams while the B plasma stream from the generator 1b is split by means of a similar brancher Tb into two streams. One of the two As plasma streams is directly guided to the portion 81a while one of the two B plasma streams is also directly conducted to the portion 81b. The other of the two As plasma streams and the other of the two B plasma streams join together in the plasma mixer S and a blended plasma consisting of As and B is produced, which is directed to the portion 81m. With this constitution, therefore, it is possible to perform the simultaneous doping.

With the conventional device of similar type in which there is used only one plasma generator, it is very difficult to dope a substrate with a plurality of impurities, even with two kinds of impurities such as As and B, in such a manner that the proportion of the doped impurities may be kept constant if the careful adjustment of the proportion in quantity of As plasma to B plasma in the generator is neglected. According to the present invention, on the other hand, a plurality of impurities to be simultaneously doped in the same area are separately turned into the corresponding plasmas, the density of each plasma is individually controlled, and thereafter each plasma stream joins another in the confluence pipe to produce a blended plasma in a predetermined blend proportion. Thus, no difficult blending of different plasmas in the fixed proportions is needed.

In addition, the use of the branching means, diverging means and scanning means as described above will make possible the control of the densities of the individual plasmas and therefore the control of blending proportion of the plasmas.

Even in case where a plurality of impurities are used, the various combination of the impurities and the control of the blending proportion will be possible by the combined use of the above described means, as described with FIGS. 3 and 4. In addition, by further branching one conducting pipe into some branched ones, as seen in FIG. 9, doping of different portions of the same substrate or of several substrates will be possible, and the control of the quantity of material doped into each portion and of doping pattern will also be facilitated.

It should here be noted that the doping of various metals with impurities can also be preformed according to the method of the present invention.

According to the method of this embodiment, the diameter of the plasma beam is as small as 3 to 4 mm due to the convergence effect of the axial magnetic field. This is especially useful for the fabrication of micro-semiconductor devices. However, in order to dope with impurities a larger area of the substrate it is sometimes preferable to increase the diameter of the plasma beam by diverting the plasma beam according to the technique described above. A mask having perforations in a predetermined shape or a slit is placed in front of the substrate so as to make possible doping in the predetermined pattern or doping in a tiny area, as in the masking method used in the conventional semiconductor technology.

As has been described, the method according to the present invention is characterized in that a great number of different doping processes can be chosen and that the proportions of the doped impurities can freely be varied. And this feature will be added to the merits of the method of transporting substance in plasma stream.

Further, if, as described with FIG. 1, a power source 3 is connected with the plasma generator 1 to maintain the plasma stream at a potential of, for example,  $V_0$  and if the receiver or the substrate 80 in FIG. 16 is grounded, then each particle of the plasma stream reaching the surface of the substrate 80 is implanted in the substrate 80 at an energy of  $eV_0$  (i.e. 400 eV when  $V_0$  is 400 V). Therefore, in case of doping a Si substrate with B atoms, the B atoms are implanted in the substrate to the depth of 14 Å. The depth of implantation is determined by the kind of ions in the plasma and

the energy of the ionized particles. If the B atoms as impurity are implanted in the depth of about 15 Å at an energy of 400 eV as above, the implanted impurities occupy all the lattice points of the Si substrate which is free of lattice defects as a result of annealing and therefore completely activated so that a very thin junction is formed on the Si substrate. Namely, the same result as obtained by the implantation of B atoms into Si substrate according to the ion beam method, can be attained.

If, as described above, impurities having energy are doped into the substrate kept at high temperatures, the impurities are implanted in the substrate to a small depth so that a great number of lattice vacancies are created in the surface of the substrate. These lattice vacancies are swiftly diffused into the inner region of the substrate due to the heat applied to the substrate so that the distribution of the concentration of lattice vacancies larger than that corresponding to the temperature of the substrate is established. This means that a domain having a diffusion coefficient greater than that corresponding to the temperature of the substrate is formed deep in the substrate. Thus, the doped impurities are subjected to enhanced diffusion. With Si substrate, enhanced diffusion takes place at temperatures in excess of 600°C and this effect multiplies as the temperature rises. Also in this case, diffusion of impurities takes place in Si substrate even if the temperature of the substrate is not so high as 1000° to 1200°C at which impurities are diffused into the Si substrate, so that the described method is applicable to the diffusion treatment required in the process of fabricating general semiconductor devices or the isolation treatment required in the process of fabricating integrated circuits, just as hot implantation in the ion implantation method is applicable to such processes.

The method according to the present invention can enjoy another effect that is also obtained by hot implantation in the ion implantation method. Namely, Si substrate is previously doped with impurities according to the method of the present invention or the conventional thermal diffusion technique and the substrate is heated. Inert neutral atoms of, for example, neon or helium are transported at an energy of 400 eV to the substrate according to the method of the present invention to generate lattice vacancies in the surface of the doped and heated substrate so that the impurities concentrated in a doped layer are subjected to accelerated diffusion due to the generated lattice vacancies.

When argon plasma is transported to the Si substrate at an energy of 300 eV, the energized argon atoms cause sputtering on the surface of the substrate. So, if this sputtering is performed on the substrate prior to the desired doping, the surface of the substrate is cleaned so that doping may be done in a preferable condition.

The method of the present invention can also perform the same thermal diffusion as carried out by the Doped Oxide method in which an oxide film containing impurities at high concentration, deposited on the substrate, is used as a source of impurities for diffusion. Namely, besides the impurities, Si and O<sub>2</sub> are turned into plasmas and the blended plasma containing the impurities, Si and O is transported to the substrate surface. Then, a SiO<sub>2</sub> film containing sufficient impurities is formed on the surface of the substrate so that the im-

purities in the SiO<sub>2</sub> film can be used as a source of impurities for diffusion.

I claim:

1. A method of transporting material to and depositing it on a target, comprising the steps of:
  - turning a first material and a second material different from said first material into respective plasmas in respective first and second plasma generator chambers, each having a small opening,
  - effusing said plasmas from said first and second chambers,
  - forming said plasmas into first and second plasma beams by means of axial magnetic fields,
  - deflecting at least one of said first and second plasma beams to join one to the other,
  - conducting the thus joined plasma beam to a desired portion of the surface of said target to make the material in said joined plasma beam deposit on said target.
2. A method according to claim 1, wherein the diameter of said joined plasma beam is increased at the immediate front of said surface of said target.
3. A method according to claim 2, wherein a mask having at least one opening is provided near the surface of said target and the material transported in said joined plasma beam is selectively deposited only on the surface of said target corresponding to said opening.
4. A method according to claim 1 wherein said target is subjected to heat treatment at deposition of said material in said joined plasma beam on said target.
5. A method according to claim 1, wherein a voltage is applied between said material in said plasma and said target in such a manner that said plasma is kept positive in potential with respect to said target.
6. A method according to claim 1, wherein said first material is zinc, said second material is magnesium and said target is an iron plate, and a thin film of zinc and magnesium is formed on said iron plate.
7. A method according to claim 1, wherein said first material is silicon, said second material is oxygen and said target is a semiconductor plate, and a compound layer of silicon and oxygen is formed on the surface of said semiconductor plate.
8. A method according to claim 1, wherein said first material is silicon, said second material is nitrogen and said target is a semiconductor plate, and a compound layer of silicon and nitrogen is formed on the surface of said semiconductor plate.
9. A method according to claim 7, which includes subsequent steps of:
  - turning a metal into plasma in a third plasma generator chamber,
  - effusing the plasma from said third chamber,
  - forming the plasma from said third chamber into a third plasma beam by means of an axial magnetic field, and
  - deflecting said third plasma beam toward said compound layer of silicon and oxygen formed on said semiconductor plate;
  - whereby a thin layer of said metal is formed on said compound layer.
10. A method according to claim 9, wherein after said metal thin layer is formed, a compound beam of silicon and oxygen is again directed to said metal thin layer to form a further compound layer of silicon and oxygen thereon.

11. A method according to claim 1, wherein said target is a semiconductor plate, said first material is a metal and said second material is oxygen, whereby a thin layer of metal oxide is formed on said semiconductor plate.

12. A method of transporting material to and depositing it on a target comprising the steps of:

turning silicon, oxygen and phosphorus into respective plasmas in respective plasma generating chambers,

effusing said respective plasmas from said respective chambers,

forming the effused plasmas into plasma beams respectively by means of axial magnetic fields,

deflecting at least two of said three plasma beams to join said three beams into a single beam, and conducting the joined plasma beam to the target which is a semiconductor plate;

whereby a compound layer of silicon, oxygen and phosphorus is formed on said semiconductor plate.

13. A method of transporting material to and depositing it on a target comprising the steps of:

turning silicon, oxygen and boron into respective plasmas in respective plasma generating chambers, effusing said respective plasmas from said respective chambers,

forming the effused plasmas into plasma beams respectively by means of axial magnetic fields,

deflecting at least two of said three plasma beams to join said three beams into a single beam, and conducting the joined plasma beam to the target which is a semiconductor plate;

whereby a compound layer of silicon, oxygen and boron is formed on said semiconductor plate.

14. A method of transporting material to and depositing it on a target of a semiconductor plate, comprising the steps of:

turning silicon, oxygen and an inert gas into respective plasmas in respective plasma generating chambers,

effusing said respective plasmas from said respective chambers,

forming the effused plasmas into plasma beams respectively by means of axial magnetic fields,

directing the plasma beam of said inert gas to a spot on the surface of said semiconductor plate to thereby clean the surface at the spot, and subsequently directing plasmas of silicon and oxygen, after joining both plasma beams into a single beam, to said cleaned spot;

whereby a compound layer of silicon and oxygen is formed on the cleaned surface of said semiconductor plate.

15. A method of transporting material to and depositing it on a target of a semiconductor plate, comprising the steps of:

turning silicon, oxygen and an inert gas into respective plasmas in respective plasma generating chambers,

effusing said respective plasmas from said respective chambers,

forming the effused plasmas into plasma beams respectively by means of axial magnetic fields,

joining the plasma beams of silicon and oxygen into a single beam,

directing the joined beam to the semiconductor plate to form a compound layer of silicon and oxygen on said semiconductor plate, and

subsequently directing the plasma beam of said inert gas to a part of the deposited compound layer to thereby remove said part of the compound layer by sputtering.

16. A method according to claim 15, which includes subsequent steps of:

turning a metal into a plasma in a further plasma generating chamber,

effusing the plasma of said metal from the chamber, forming the effused plasma into a plasma beam by means of an axial magnetic field, and

directing the plasma beam of said metal to an opening made in said compound layer by said sputtering with the plasma beam of the inert gas to thereby deposit said metal in said opening.

17. A method of transporting material to and depositing it on a substrate comprising the steps of:

generating at least two plasma beams of at least one substance;

joining together said generated plasma beams to form a joined plasma beam;

guiding said joined plasma beam to at least a part of one surface of said substrate; and

forming a layer of said at least one substance on said part of one surface of said substrate.

18. A method according to claim 17, wherein each of said plasma beams is formed of an identical substance.

19. A method according to claim 17, wherein each of said plasma beams is formed of a different substance.

20. A method according to claim 19, wherein said layer is a compound of said different substances.

21. A method according to claim 20, wherein said substrate is a single crystal.

22. A method according to claim 21, wherein said layer of said compound is a single crystal layer of said compound.

23. A method according to claim 21, wherein said single crystal substrate is a semiconductor material.

24. A method according to claim 23, wherein said at least two plasma beams consist of a first and second plasma beams, each of said first and second plasma beams being formed of a respective first and second material.

25. A method according to claim 24, wherein said first material is the same semiconductor material as said single crystal substrate and said second material is a conductivity determining material for said semiconductor material.

26. A method according to claim 17, wherein said plasma beams are guided by means of magnetic pipes.

27. A method according to claim 26, wherein said magnetic pipes include at least one bend such that neutral particles existing in said plasma beams are removed.

28. A method according to claim 17, wherein said joined plasma beam is at a positive potential with respect to said surface.

29. A method according to claim 28, wherein said positive potential is 400 eV or less.

30. A method according to claim 17, wherein said step of guiding further includes branching said joined plasma beam into a plurality of plasma beams.

31. A method according to claim 30, wherein said at least a part of one surface includes a plurality of differ-

ent surface portions, each of said plurality of plasma beams being guided to a respective one of said plurality of different surface portions.

32. A method according to claim 30, wherein each of said plurality of plasma beams is further guided to a respective different location at said one surface.

33. A method according to claim 17, wherein said surface is heated during the step of forming said layer.

34. A method according to claim 33, wherein said surface is heated to a temperature of about 500°C.

35. A method according to claim 33, wherein said surface is heated to a temperature of between about 1000° to 1200°C.

36. A method of transporting material to and depositing it on a substrate comprising the steps of:

generating at least one plasma beam of at least one substance;

guiding said at least one plasma beam to at least one substrate including branching said at least one plasma beam into a plurality of plasma beams; and forming a layer of said at least one substance at each of a plurality of locations.

37. A method according to claim 36, wherein said at least one substrate includes a plurality of different substrates, each of said plurality of plasma beams being further guided to a respective one of said plurality of different substrates.

38. A method according to claim 36, wherein each of said plurality of plasma beams is guided to a respective different location at said at least one substrate.

39. A method of transporting material to and depositing it on a substrate comprising the steps of:

generating a first material into a first plasma in a first plasma generating chamber having a small opening;

generating a second material into a second plasma in a second plasma generating chamber having a small opening;

effusing each of said generated plasmas through each of said small openings by force of a difference in plasma density;

forming each of said effused plasmas into respective plasma beams by means of magnetic pipes provided by axial magnetic fields;

transporting said respective plasma beams through said magnetic pipes;

joining together said transported plasma beams to form a joined plasma beam;

directing said joined plasma beam to at least one part of one surface of said substrate; and

forming a layer of said first and second materials on said at least one part of one surface of said substrate.

40. A method according to claim 39, further comprising the step of widening said joined plasma beam.

41. A method according to claim 40, wherein said step of widening said joined plasma beam includes adjusting the corresponding axial magnetic field.

42. A method according to claim 39, further comprising the step of branching said joined plasma beam during said step of directing by adjusting the corresponding axial magnetic field, thereby causing widening of the cross-section of said joined plasma beam to allow divergence of separate branches of said plasma beam to be formed by components of the corresponding axial magnetic fields.

43. A method according to claim 39, further comprising the step of branching at least one of said plasma beams prior to said step of transporting.

44. A method of transporting material to and depositing it on a substrate comprising the steps of:

turning a first and a second material into respective plasmas respectively in a first and a second chamber, each of said chambers having a small opening; effusing each of said respective plasmas through each of said small openings;

forming each of said respective plasmas into respective plasma beams by means of axial magnetic fields;

joining together said respective plasma beams to form a joined plasma beam;

directing said joined plasma beam to the surface of a single crystal substrate; and

forming a single crystal of a compound consisting of said first and second materials on said single crystal substrate.

45. A method according to claim 44, wherein said single crystal substrate is GaAs, said first material is gallium and said second material is arsenic.

46. A method according to claim 44, wherein said single crystal substrate is a semiconductor, said first material being the same semiconductor material as said substrate, and said second material being one for determining the conductivity of said semiconductor when added thereto.

47. A method according to claim 44, wherein said substrate is subjected to heat treatment at a temperature higher than 500°C when a single crystal of said materials is grown on said substrate.

48. A method according to claim 44, wherein a predetermined voltage is applied between each of said plasmas and said substrate in such a manner that each of said plasmas is kept more positive than said substrate in potential.

49. A method according to claim 44, wherein a mask having at least one opening of a desired pattern is disposed between said joined plasma beam and said substrate.

50. A method according to claim 49, wherein said mask is a SiO<sub>2</sub> layer formed directly on the surface of said substrate.

51. A method of transporting material to and depositing it on a substrate comprising the steps of:

turning silicon, oxygen and an impurity material into respective plasmas respectively in first, second and third plasma generating chambers, each of said chambers having a small opening;

effusing each of said respective plasmas through each of said small openings;

forming each of said respectively effused plasmas into respective plasma beams by means of axial magnetic fields;

joining together said plasma beams to form a joined plasma beam;

directing said joined plasma beam to the surface of the substrate; and

forming a compound layer of silicon and oxygen containing said impurity material on said surface of the substrate.

52. A method according to claim 51, wherein said substrate is subjected to heat treatment.

53. A method according to claim 51, wherein said compound layer is a single crystal of silicon and oxygen containing said impurity material.

54. A method according to claim 51, wherein said compound layer is formed to a predetermined thickness.