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54] **METHOD OF GROWING FROM SOLUTION MATERIALS EXHIBITING A PELTIER EFFECT AT THE SOLID-MELT INTERFACE**

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51] **Int. Cl.** **H01l 7/38**

58] **Field of Search** 148/171–3, 148/1.5, 1.6; 204/39, 61; 117/201

56] **References Cited**

UNITED STATES PATENTS

,999,776	9/1961	Dorendorf et al.	148/1.6
,145,125	8/1964	Lyons	148/175
,411,946	11/1968	Tramposch	117/201
,611,069	10/1971	Galginaitis et al.	148/171 X
3,676,228	7/1972	Sakurai et al.	148/171

OTHER PUBLICATIONS

Kumagawa et al., J. Electrochem. Soc.: Solid State Science," Vol. 120, No. 4, April 1973, pp. 583 and 584.

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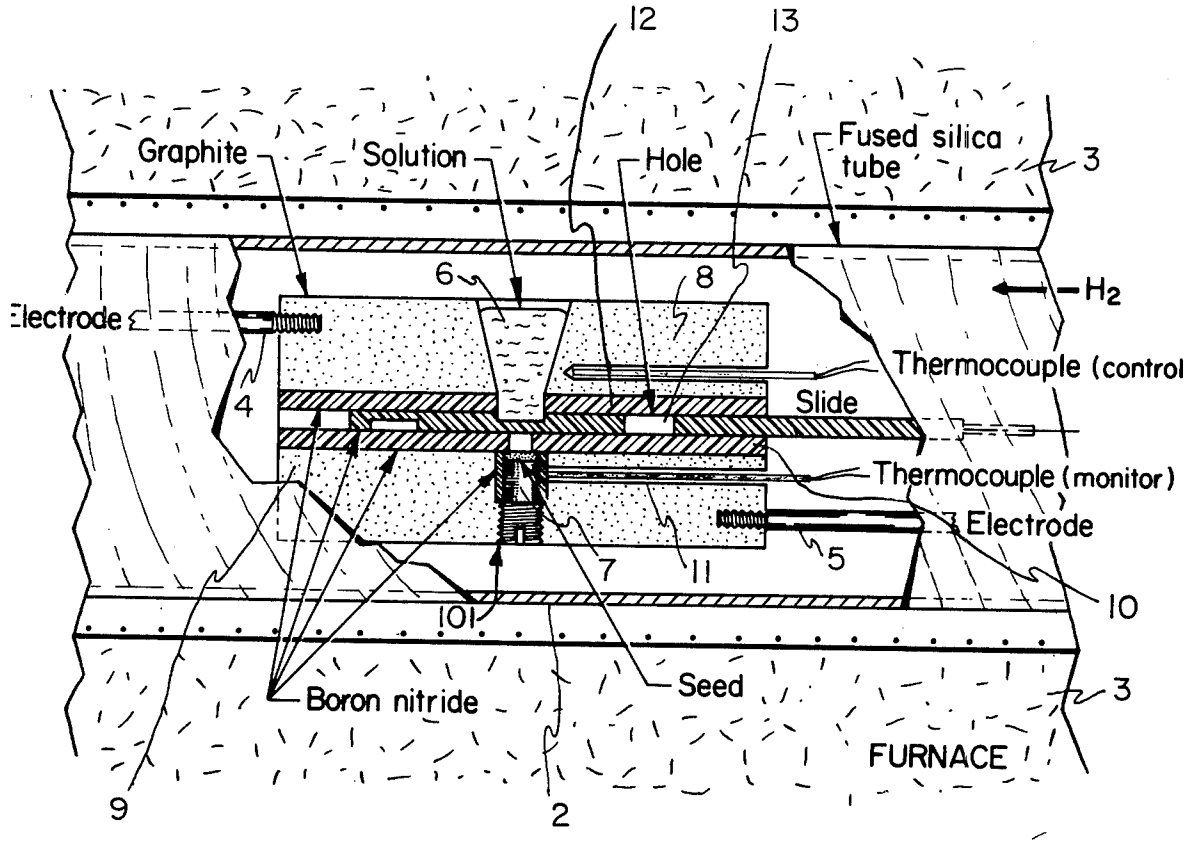
[57] **ABSTRACT**

A method of growing epitaxial layers from a solution in a solution-substrate system. An electrically conductive solution, consisting of one or more materials to be deposited upon the substrate, is placed in contact with the substrate. The temperature of the system is established and maintained at a level at which the solution is at or near saturation. An electric current is then passed across the interface between the solution and the substrate, the direction and magnitude of the current being chosen to effect cooling at the interface only, the remainder of the system being maintained at said equilibrium temperature.

25 Claims, 4 Drawing Figures



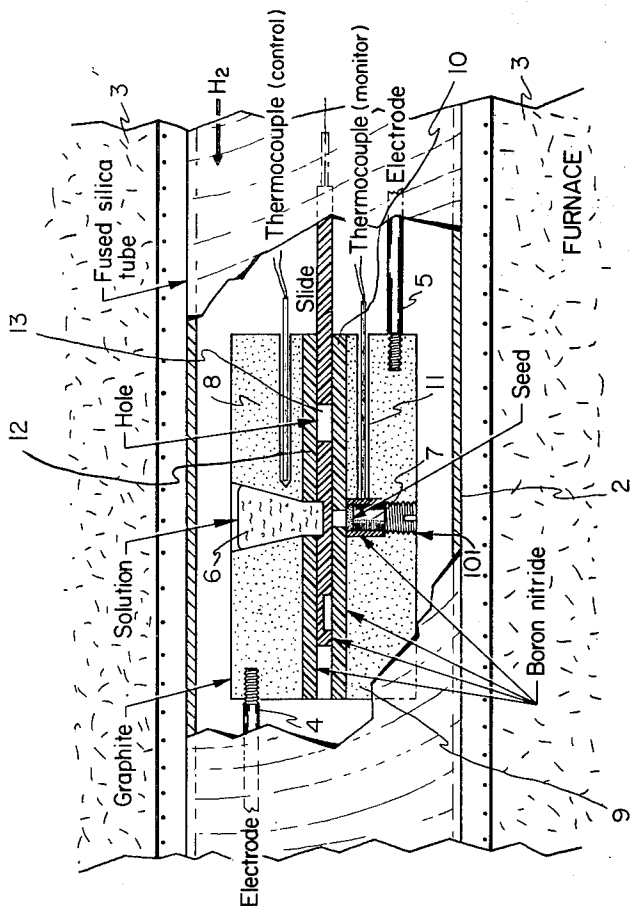

Fused silica tube
H2
Thermocouple (control)
Thermocouple (monitor)
Electrode
FURNACE
Slide
Hole
Seed
Solution
Boron nitride
Graphite
Electrode
3
10
5
13
8
11
12
7
2
6
101
4
9

FIG. 1

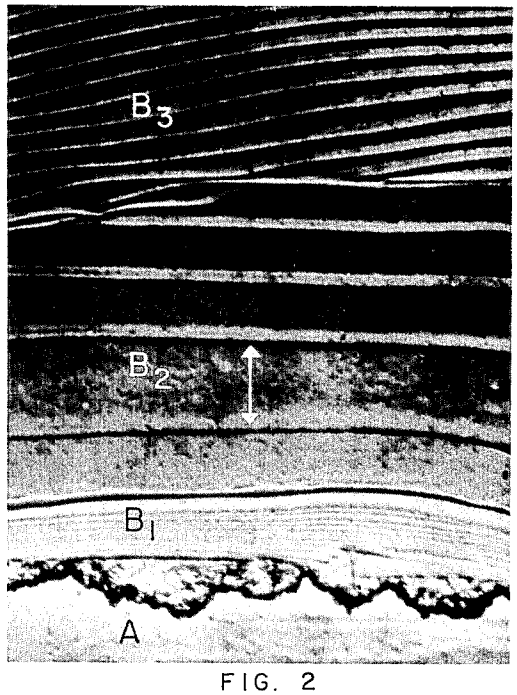

B3
B2
B1
A

FIG. 2

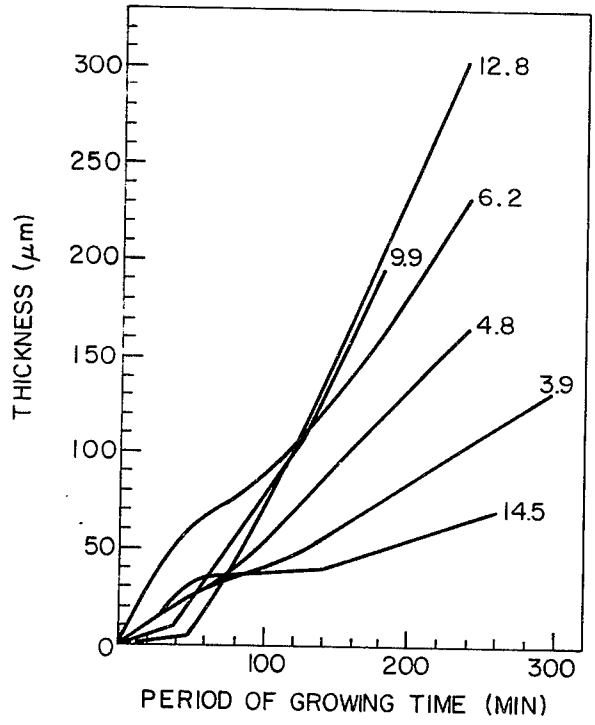

300
250
200
150
100
50
0
THICKNESS (μm)
12.8
6.2
9.9
4.8
3.9
14.5
100
200
300
PERIOD OF GROWING TIME (MIN)

FIG. 3

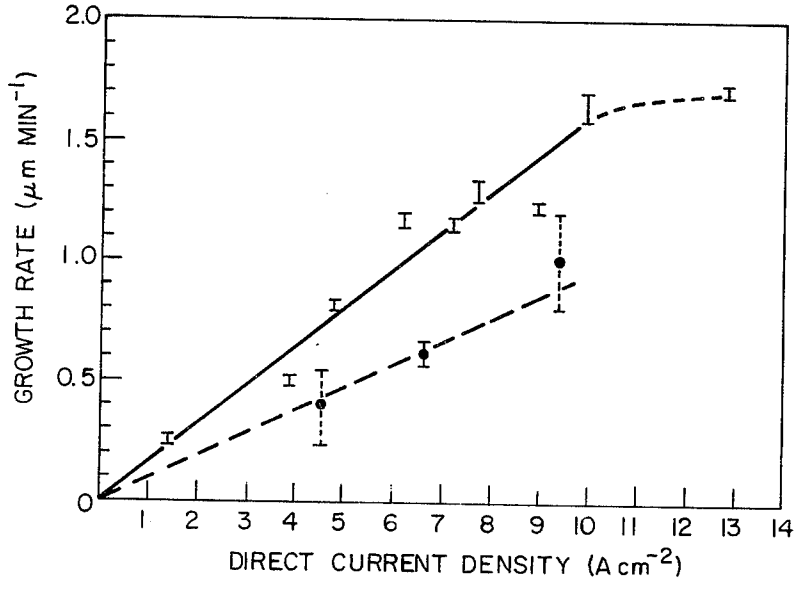

2.0
1.5
1.0
0.5
0
GROWTH RATE (μm MIN⁻¹)
1 2 3 4 5 6 7 8 9 10 11 12 13 14
DIRECT CURRENT DENSITY (A cm⁻²)

FIG. 4

METHOD OF GROWING FROM SOLUTION MATERIALS EXHIBITING A PELTIER EFFECT AT THE SOLID-MELT INTERFACE

The invention described herein was made, in part, in the course of a grant from the National Science Foundation, an agency of the United States Government.

The present invention relates to a method of growing epitaxial layers from a solution in a solution-substrate system and, in particular, to a method that employs local cooling at the interface between the solution and the substrate of such system by Peltier cooling.

In a journal article entitled "Modulation of Dopant Segregation by Electric Currents in Czochralski-Type Crystal Growth," J. Electrochem. Soc.: SOLID STATE SCIENCE, June 1971, pp. 1013–1015, the present inventors discuss dopant segregation in tellurium-doped, indium antimonide single crystals by electric currents applied across the growth interface during Czochralski-type crystal growth. The authors employed electric current pulses of short duration to effect time marking during crystal growth, and to allow observation of growth rates under differing growth conditions.

In a further journal article entitled "Current-Controlled Growth and Dopant Modulation in Liquid Phase Epitaxy," by the present inventors and another, J. Electrochem Soc.; SOLID STATE SCIENCE, April 1973, pp. 583–584, there is described work by the present inventors in connection with crystal growth in a solution-substrate system of the type hereinafter discussed and amplified upon and wherein thermal equilibrium of the system is established.

Most semiconductor devices used are junction devices. Most such devices are fabricated using diffusion techniques. Such techniques result in junctions which are not usually abrupt, i.e., they have a slope, which fact has a large effect upon the performance of such devices. Abrupt junctions are particularly important in light-emitting diodes (e.g., GaP), solar cells (e.g., GaAs) and the like. It is an object, therefore, of the present invention to provide a process for growing epitaxial layers in which the dopant profile of a junction can be controlled to provide a steep dopant profile at the junction.

A further object is to provide a method of growing semiconductor devices by a method that is much faster than previously-known methods.

A still further object is to provide such devices with controlled distribution of dopant and, accordingly, more uniform properties.

A still further object is to provide such devices with controlled variations of composition.

These and still further objects are evident in the discussion that follows and are particularly delineated in the appended claims.

The objects of the invention are attained by a method of growing epitaxial layers from a solution-substrate system, in which the system as a whole is maintained at or near the saturation temperature of the solution but in which the temperature of the interface between the solution and the substrate is controlled by an electric current passed across the interface. To accomplish the desired growth, an electrically conductive substrate (or a seed) is placed in contact with a conductive solution containing onee or more materials to be deposited upon the substrate. The temperature of the solution and the substrate is established and maintained at a level at which the solution is saturated. An electric current is passed across the solution-substrate system in such a way that cooling is effected at the interface between the solution and the substrate, the cooling occurring only during the time in which electric current flows across the interface and only at the region of said interface. The rest of the solution-substrate system, except said interface, is maintained at the temperature that existed prior to applying the electric current.

The invention is hereinafter discussed with reference to the accompanying drawing in which:

FIG. **1** is a schematic representation of apparatus operable to perform the method of the present invention and adapted, among other things, to pass an electric current across the interface of a liquid-solid to effect epitaxial growth at the interface;

FIG. **2** is a photomicrograph (X470) of an epitaxial layer of InSb grown by the present method;

FIG. **3** is a graph of thickness of growth of an epitaxial layer as a function of time and current density across the interface, the layer having the composition of Example **3** hereof; and

FIG. **4** is a graph of growth rate as a function of current density across the interface for the composition of Example **3.**

There follows now a short explanation of the apparatus designated **101** in FIG. **1**, which was employed by the present inventors to grow semiconductor layers from a solution in a solution-substrate system. Epitaxial layers of the type hereinafter noted are grown in a region of controlled atmosphere **1** (e.g., hydrogen) within a silica tube **2.** The tube **2** in the actual apparatus used is contained within in an electric furnace **3** which provides a controllable ambient temperature. Electric current to provide the Peltier effect herein discussed is supplied through electrodes **4** and **5** from a d-c supply (not shown). A solution **6** consisting of one or more materials to be deposited upon a substrate (or a seed) **7**, is contained within a cavity in an upper graphite element **8.** The substrate **7** is held by a lower graphite element **9** which is also the electrical contact thereto. The upper and lower graphite elements are insulated from one another by an insulating slide **10** which is movable horizontally between insulating elements **11** and **12** (e.g., boron nitride). With the slide **10** in the position shown, the solution and the seed are electrically isolated from one another. For the growth process, the slide **10** is moved to the left in order that the hole labeled **13** register with the seed and the solution. At this juncture, the temperature of the working parts of the apparatus are such that the solution is at or near saturation.

With the solution and substrate in contact with one another, an electric current is passed across the interface therebetween in such a way that cooling is effected at said interface. The direction of current flow to effect such cooling depends upon the materials to be deposited. For the InSb system later discussed, such electric current flow is from the substrate **7** to the solution **6.** The rate of deposition is dependent upon and directly proportional to the current density at the interface.

It will be appreciated from the above explanation that the cooling due to the electric current is localized to the interface region between the solution **6** and the substrate **7,** that such cooling occurs only during the passage of the electric current, and that the remainder of the solution-substrate system, except said interface is maintained at or close to the original temperature. I

will be appreciated that, conceptually, one could start the present process with a solution alone, the necessary substrate being formed on a conducting electrode (e.g., carbon) in contact with the solution, the epitaxial layers thereafter being grown in the manner herein described. Care must be taken to minimize Peltier heating at the surface of the electrical contact between the substrate **7** and the electrode contact thereto.

EXAMPLE 1

The InSb epitaxially-grown material in FIG. **2** was grown from an indium solution consisting of 60 atomic percent indium and 40 atomic percent antimony. The solution contained tellurium as a dopant to provide growth marks in accordance with the teaching in the June 1971 journal article. The InSb layer was grown on an InSb substrate. The solution-substrate system was established and maintained at 470°C, at which temperature the solution is at or near saturation for this particular composition. At that temperature a small amount of the substrate may be dissolved in the solution and a flat interface forms between the solution and the substrate. The three growth regions B_1, B_2 and B_3 in FIG. **2**, were obtained by passing a continuous current of 0, 5.5, and 1 ampere per cm^2, respectively, through the growth interface. In all three regions, rate striations (as discussed in the June 1971 journal article) were introduced by superimposing current pulses of 0.1 second duration (100 amperes/cm^2) at a repetition rate of 0.01, 0.02, and 0.02 seconds, respectively.

The growth irregularities upon transition from regions B_2 and B_3 (changing interface morphology) are as yet unexplained, in work done to date, and are subject to further investigations. It is seen that in the first growth region (B_1) where only intermittent pulses were applied but no "base current" was passed, the growth was very limited. Over a period of 5000 seconds an epitaxial layer of a total thickness of **25**μm was intermittently formed (due to cooling brought about by the pulses) at a net growth rate of $3 \times 10^{-1}\mu$m/minute. A base current of 5.5 A/cm^2 for a period of 1200 seconds (middle region) led to a layer (B_2) of a total thickness of 125μm at an everage growth rate of about **6**μm/minute. It should be noted that in this region of growth rate during the superposition of each pulse was about 4000μm/minute (as determined from the width of the rate striations associated with the 0.1 seconds pulse duration), i.e., about 670 times greater than the average growth rate. The epitaxial region obtained as a base current density of 1 A/cm^2 (B_3 in FIG. **2**) grew at an average rate of 3μm/minute; during the superposition of the pulses the rate was approximately 1500μm/minute.

In the region grown at a base current of 5.5 A/cm^2 the rate striations resulting from the pulses appear as bands rather than lines. This result reflects a high growth rate induced by the base current, the growth rate being further increased by a factor of close to 700 for the duration of each high current density pulse. The sudden increase in growth rate leads to a substantial increase in dopant concentration, which in turn is attenuated within the duration of the pulse, because of boundary layer depletion. Such segregation behavior was indeed observed during said work through the etching characteristics of the bands which reveal pronounced concentration increases at their lower edge (beginning of pulse) and gradual transitions on their upper edge (termination of pulse). Thus, controlled modulation of cheemical composition may be achieved by the appropriate choice of pulse shape and duration.

In Example 1, the matrix material is indium antimonide and the dopant is tellurium. The matrix material has a solidification point which is determined by the percent of indium and antimony. For any particular composition, the rate of deposit of the matrix material and of the dopant can be varied up or down by increasing or decreasing, respectively, the electric current density at the interface. Furthermore, in the ranges of values used and in all work done so far, both the rate of crystal growth and the concentration of incorporated dopant relate directly to the current density, as approximately linear functions which differ in their slopes. Thus, the dopant concentration or concentrations can be varied such as, for example, to form a junction. In addition, if two or more dopants are placed in the solution, the rates of deposition of each will vary as a function of the current density; so the ratio of the concentration of dopants in the layer can be modified. It should be noted, in this connection, that the percent tellurium in the deposited layer increases with increasing current density, but in the case of other dopants the dopant concentration in the layer may increase or decrease depending upon the particular dopant--and the change can be pre-determined.

EXAMPLE 2

Epitaxial growth of the crystals of InSb was also achieved from solution at a furnace temperature of 510°C; the solution consisted of 68 atomic percent antimony, 32 atomic percent indium, and small amounts of tellurium to allow growth marking. The growth rates were consistent with the rates noted above in connection with Example 1.

EXAMPLE 3

Epitaxial growth of crystals of InSb was also achieved from an indium solution at a furnace teemperature 460°C; the solution consisted of 75 atomic percent indium, 25 atomic percent antimony, and small amounts tellurium as a dopant for revealing rate striations, as before. The d-c current flow was again from substrate to solution and there were imposed upon this steady current pulses of 0.5 second duration and of 105 amperes/cm^2 density to provide said striations. Thickness of material grown as a function of current density through the liquid-solid interface for the materials of Example 3 are shown in FIG. **3** and the growth rate as a function of current density is shown in FIG. **4**. The upper (solid) curve in FIG. **4** shows the growth rate, current-density relationship observed under steady-state growth; the vertical lines represent experimental deviations. the lower (broken) curve in FIG. **4** shows the growth-rate, current-density relationship observed under transient growth conditions; the vertical lines reflect deviation in growth rate observed for a given current density (under non-steady-state conditions).

In the foregoing systems the resulting solid is an n-type semiconductor which can be changed to n^+ by modifying the tellurium concentration, thereby to form an n—n^+ structure. As before indicated, the concentration of tellurium is increased by increasing the current density across the junction (i.e., increasing the growth rate) and vice versa. Junctions are formed by abrupt changes in current density. Junctions of the p-n type can be formed by providing a matrix material (e.g., in-

dium and antimony) and one or more dopants; the concentration of the constituents of the matrix, the dopants chosen, and the relative concentration of the dopants are such as to permit dopant concentration in the solid matrix to be affected by changes in the current density at the liquid-solid interface. The present method is useful for matrix compositions consisting of group III–V systems and dopants from group IV elements (e.g., germanium and silicon); some of these matrix materials change from *n* to *p* on the basis of the concentration of a single dopant present. Thus, a compound matrix and single-element dopant can be formed into a p-n junction by the instant technique, by changing abruptly the current density at the liquid-solid interface. GaAs is an example of a compound matrix which can be changed by a change in the concentration of a dopant such as germanium or silicon for example.

In the foregoing explanation, the current is unidirectional. The current can be increased for a time and then decreased for a time, or vice versa, to provide a particular profile of growth and/or dopant concentration, but it is always in one direction. And the variation in current density can be at a uniform rate or a non-uniform rate, as desired.

Further modifications of the invention herein disclosed will occur to persons skilled in the art, and all such modifications are deemed to be within the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

1. A method of growing epitaxial layers from a solution in a solution-substrate system, said system comprising materials that exhibit Peltier effect at interface between the solution and the substrate, that comprises: placing a conductive substrate in contact with a conductive solution which initially comprises a solvent and one or more materials to be deposited upon the substrate, establishing and maintaining the solution and the substrate at a temperature at which the solution is liquid and is at or near saturation, passing an electric current across the solution-substrate system in such a way that cooling is effected at the interface between the liquid solution and the substrate, said cooling occurring only during the time in which electric current flows across the interface and only at the region of said interface, the rest of the solution-substrate system, except said interface, being maintained at the temperature that existed prior to the passage of the electric current, and controlling the magnitude of the electric current to control the current density at said interface.

2. A method as claimed in claim **1** in which the conductive solution comprises said solvent and a single, elemental or the constituents of a stoichiometric-compound material to be deposited and in which the density of the electric current at the interface is controlled to establish a desired rate of deposition of the material.

3. A method as claimed in claim **2** in which the current density at the interface is varied to change the rate of deposition.

4. A method as claimed in claim **3** in which the current density is varied at a uniform, unidirectional rate to establish a desired change in the deposition rate.

5. A method as claimed in claim **3** in which the current density is varied abruptly at a predetermined time during growth to form a junction.

6. A method as claimed in claim **1** in which the conductive solution contains a plurality of materials to be co-deposited and in which the density of the electric current at the interface is controlled to establish a desired deposition rate for each material of the plurality of materials.

7. A method as claimed in claim **6** in which the current density at the interface is varied at a predetermined uniform, unidirectional rate to establish a uniform change in the deposition.

8. A method as claimed in claim **6** in which the current density at the interface is varied abruptly at a predetermined time during growth to form a semiconductor junction.

9. A method as claimed in claim **1** in which one of said materials in the solution is a matrix material and another of said materials is a dopant, the matrix material and the dopant being co-deposited on the substrate and the rate of co-deposition of each being controlled by controlling the current density at the interface.

10. A method as claimed in claim **9** in which the current density at the interface is varied at a predetermined uniform undirectional rate to establish a uniform change in the composition of the deposited material.

11. A method as claimed in claim **9** in which the current density at the interface is varied abruptly at a predetermined time during growth to form a semiconductor junction.

12. A method as claimed in claim **9** in which said materials in the solution comprise a plurality of dopants and in which the current density at the interface is controlled to control the rate of deposition of each dopant.

13. A method as claimed in claim **12** in which the current density at the interface is varied at a predetermined uniform unidirectional rate to establish a uniform change in the composition of the deposited material.

14. A method as claimed in claim **12** in which the current density at the interface is varied abruptly at a predetermined time during growth to form a semiconductor junction.

15. A method as claimed in claim **1** in which the materials in the solution include a matrix material and a plurality of dopants, the concentration of the dopant impurities in the solution being chosen so that appropriate current density changes at any time during growth will be effective to cause one dopant to predominate in terms of rate of deposition.

16. A method of growing a semiconductor epitaxial layer from a solution, that comprises: bringing a seed in contact with a conductive liquid solution which initially contains a solvent and a material to be deposited upon the seed to form the layer, establishing and maintaining the solution and the seed at a temperature at which the solution is at or near saturation, passing an electric current through the interface region between the solution and the seed in such a way that cooling is effected at the interface, said cooling occurring only during the passage of said electric current and only at the region of said interface, the rest of the solution-seed system, except said interface, being maintained at said temperature, and controlling the magnitude of the electric current to control the current density at said interface, thereby to control growth of the layer.

17. A method as claimed in claim **16** in which the conductive solution contains said solvent and a single, elemental or stoichiometric compound material to be

deposited and in which the density of the electric current at the interface is controlled to establish a desired rate of deposition of the material.

18. A method as claimed in claim **16** in which the conductive solution contains a matrix material and at least one dopant.

19. A method of growing an epitaxial layer from a solution that initially contains a solvent and one or more materials to be deposited to form said layer, that comprises: establishing and maintaining the solution at a temperature at which it is liquid in form, said temperature being substantially the saturation temperature for the particular composition of the liquid, reducing the temperature of a region of the liquid to a level at which solidification occurs, passing an electric current through the interface area between the solution and the solid thus formed in a direction to effect cooling at the interface area, said cooling occurring only during passage of said electric current and only at the area of said interface, the rest of the growth system, except said interface, being maintained substantially at said saturation temperature, and controlling the magnitude of the electric current to control the current density at said interface.

20. A method as claimed in claim **19** in which said composition comprises materials which form a semiconductor upon solidification.

21. A method as claimed in claim **20** in which the electric current is d-c and in which at a predetermined time the level of current is changed abruptly to effect formation of a semiconductor junction.

22. A method as claimed in claim **21** in which said materials are indium, antimony and the dopant tellurium.

23. A method as claimed in claim **21** in which said materials comprise group III–V systems which form a matrix material and at least one group IV element as a dopant.

24. A method as claimed in claim **23** in which the matrix material and dopant are adapted to form either a p-type semiconductor or an n-type semiconductor, depending upon the concentration of dopant in the solid, and in which the ratios of material constituents in the solution are chosen and current densities are regulated to grow the semiconductor in the form of a p-n junction.

25. A method as claimed in claim **24** in which the group IV element dopant is either germanium or silicon.

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