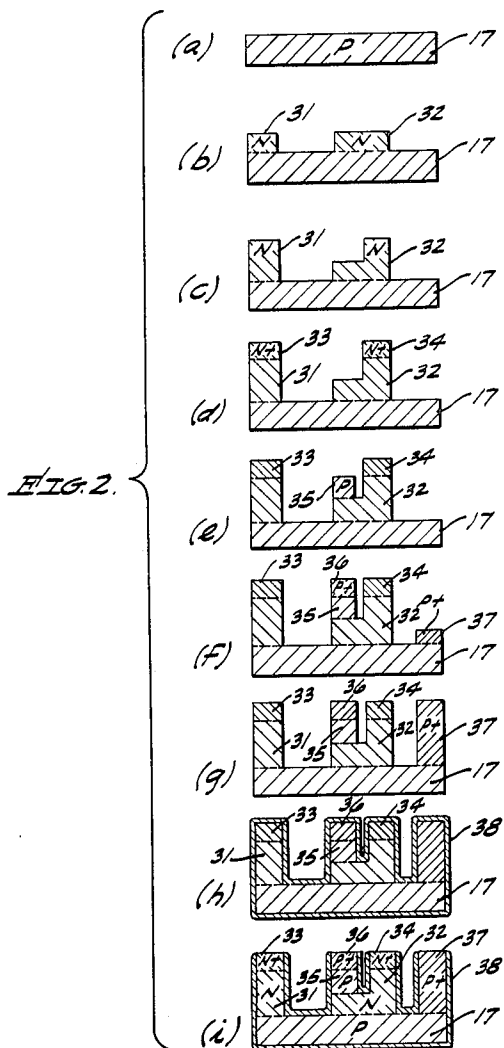
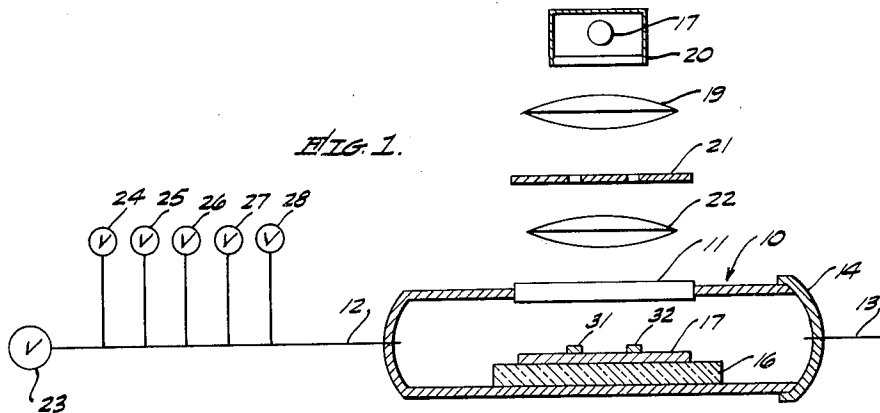


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FOCUSING ELECTROMAGNETIC RADIATION
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CONTROLLED EPITAXIAL CRYSTAL GROWTH BY FOCUSING ELECTROMAGNETIC RADIATION

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This invention relates to controlled epitaxial crystal growth, and more particularly to a method for sustaining the growth process within a defined area on a desired substrate.

Vapor growth is a process of growing a solid material from a suitable atmosphere on a substrate. The growth is epitaxial when the material grown forms an extension of the crystal structure of the substrate. Vapor growth processes which form such epitaxial layers are popularly called epitaxial growth processes and the atmosphere used for such vapor growth processes is called an "epitaxial growth atmosphere." A variety of vapor growth processes capable of producing epitaxial layers on crystalline substrates are known and are generally classified as disproportionation processes, reduction processes and thermal decomposition processes. Such processes have been used to deposit semiconductor materials upon crystalline substrates, as illustrated in U.S. Patents to R. C. Sangster, 2,895,858 and to Christensen et al. 2,692,839. By the addition of gases comprising donor or acceptor type impurities, the epitaxially deposited layer may be made to be N-type or P-type as desired.

In the production of particular devices, it would be desirable to delineate or control the area on a substrate upon which the growth processes proceed. With such control it would be possible to produce a variety of devices having successively deposited layers of different conductivity, or on different areas of the substrate. Such control has been proposed by the use of jigs, or masks, to cover the portion of the substrate where it is desired to inhibit growth, so that upon exposure to the growth atmosphere and conditions, growth will take place only on the unmasked portions of the substrate. Where successively grown layers are desired, it has been necessary to exchange one mask for another between successive vapor growth periods. The procedures for the exchange of masks require manipulations during which the atmosphere surrounding the substrate is disturbed. Surface oxidation may occur to an extent requiring subsequent removal of the oxide before the second growth period may commence. The present invention provides for successive growth periods for producing epitaxial layers in successive areas without risk of intermediate oxidation or contamination of previously deposited epitaxial layers.

It has been found that the rate of vapor growth of an epitaxial layer on the substrate material from a gas phase molecule depends upon the following factors:

- The partial pressure of the reducing species;
- The partial pressure of any oxidizing species;
- The concentration of free radicals;
- The activation energy of the reactions;
- The temperature on the substrate surface; and
- The partial pressure of the substrate species compound which is ultimately reduced and deposited as an epitaxial layer.

In the thermal decomposition process the temperature is raised sufficiently high that the activation energy for the growth process is exceeded by a sufficiently large percentage of the reaction collisions to produce a useful growth rate. The reaction is generally believed to in-

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volve free radical mechanics wherein the activation energy for the reaction is the energy required to produce and propagate the free radicals themselves. In practice substantially uniform heating of crystalline substrates results in the producing of uniformly thick epitaxial layers over the entire surface which is exposed to the epitaxial growth atmosphere.

It has been found that a crystalline substrate upon which an epitaxial layer is to be grown may be held at a temperature just below that which is sufficient to activate the growth processes and the remaining energy, or driving force, for the reaction may be produced by delivering electromagnetic radiation on to the substrate on the area where growth is desired. The rate of growth on the irradiated area of the substrate may be determined by the intensity of and the distribution of the radiation.

The preferred method for delivering and controlling the electromagnetic radiation to produce the desired driving force in a defined area is to place the substrate upon which growth is desired adjacent a window in a furnace chamber through which a suitable growth atmosphere is passed, to position a light source and an optical system adjacent the window and outside the chamber to deliver the desired radiation energy through the window and onto the substrate. The optical system may comprise the light source, an adjacent condensing lens, and a mask between said lens and the window to define the areas on the substrate to be irradiated. An additional lens between the mask and the window is desirable where the configuration of the areas on the substrate is of a definite size, generally much smaller, than the configuration of the apertures in the mask through which the radiation passes.

As a specific example of controlled area growth by activation of vapor growth through electromagnetic radiation, a germanium crystal substrate is deposited in a windowed chamber through which is passed an atmosphere consisting essentially of GeCl_4 and GeCl_2 as reactants, H_2 as a reducing agent, HCl as an inhibiting agent, helium or argon as an inactive diluent and AsCl_3 as a doping agent. The substrate and the adjacent atmosphere are heated to a temperature within about 50°C . below the thermal reaction temperature at which the vapor growth process will proceed, and an ultraviolet light source is activated to deliver through the window sufficient ultraviolet light to provide the activation energy adjacent to the substrate required to sustain the epitaxial growth process. The resulting layer of epitaxial material will be N-type germanium whose conductivity is proportional to the percentage of AsCl_3 which was present in the vapor growth atmosphere.

For further consideration of what is believed to be novel and my invention, attention is directed to the drawings in which:

FIG. 1 is a schematic illustration of an apparatus for producing vapor growth according to the present invention; and

FIG. 2 is a schematic illustration showing successive layers deposited upon a substrate to produce a semiconductor device.

FIG. 1 is a schematic illustrative showing of apparatus for maintaining a crystalline substrate, such as a slice of P-type germanium on a support or jig, in a heated chamber at a temperature and in an epitaxial growth atmosphere such that the activation energy for the vapor growth process is just insufficient for substantial growth. An optical system is utilized to deliver electromagnetic radiation, in this case ultraviolet light, through a mask and a window and onto the substrate to locally increase the activation energy adjacent the substrate surface and thus to induce localized crystal growth.

As shown in FIG. 1 a furnace chamber 10 whose

temperature control apparatus is not shown in provided with a window 11 (which may be quartz) and atmosphere inlet and outlet 12 and 13. Access to the chamber is preferably through a removable end cap 14 for purposes of loading and discharging jigs and work thereon. A quartz jig 16 supports a germanium crystal slice 17 the size of which is exaggerated in size for purposes of illustration. An optical system is illustrated comprising a light source 18 having a light filter 20 for passing ultraviolet light, a condensing lens system 19, a mask 21 and a focusing lens system 22 which is preferably designed to focus a reduced image of the apertures in the mask 21 upon the surface of the substrate 17.

In operation of the apparatus of FIG. 1, a jig 16 with germanium P-type slice 17 thereon is charged through the end cap 14 into the furnace chamber 10 and positioned adjacent to window 11. The furnace chamber is suitably purged, with hydrogen gas supplied through valve 24, and the furnace chamber with the work therein is raised to a temperature of approximately 700° C. to reduce oxides, then reduced to 450° C, or about 50° C below the temperature at which reduction of GeCl_4 takes place. As the temperature of the chamber approaches the holding temperature of about 450° C, and epitaxial growth atmosphere for growth by the hydrogen reduction process is established in the chamber by supplying thereto a gas mixture consisting essentially of hydrogen as a carrier and reducing gas, germanium tetrachloride through valve 25 as the germanium source gas, and, a minor percentage of arsenic trichloride gas through valve 28 of the order of 1% of the amount of germanium tetrachloride supplied. The light source 18 is energized and the ultraviolet electromagnetic radiation therefrom is focused upon the crystal slice to locally activate the crystal growth process. It is believed that the irradiation with ultraviolet light supplies sufficient energy at the crystal surface to produce free radicals in the atmosphere of H_2 , GeCl_4 , GeCl_3 , GeCl_2 , Cl together with other free radicals in lesser concentrations. Sufficient AsCl_3 enters into the free radical mechanism to insure the deposit in the germanium epitaxial layer of arsenic impurity, thus making the layer N-type. A neutral or inactive diluent gas such as argon or helium may be supplied to the furnace chamber through valve 24 to help control the diffused spreading of the gas phase reaction and thus localize and control the epitaxial growth in the irradiated surface areas.

When a sufficient period of time has elapsed for growth of N-type germanium (arsenic doped) to the desired thickness, as for example producing epitaxial regions 31 and 32 in FIG. 1, the ultraviolet light source 18 may be inactivated, the AsCl_3 gas supply may be turned off by the valve 28, and a boron trichloride gas supply turned on at valve 27. After sufficient time for purging the atmosphere in the chamber and establishing the boron trichloride containing atmosphere, the light source 18 is turned on and the growth process is continued. If desired a new mask may replace the mask 21 so that the succeeding areas of growth are somewhat different than the areas as activated through the mask 21. As the vapor growth process proceeds with the boron trichloride impurity in the atmosphere, an epitaxial layer of P-type germanium is grown on the crystal slice 17. By suitable adjustment of the impurities or dopant materials in the atmosphere, and by planned changing of masks, complex structures may be deposited and grown upon crystalline substrates. Light and heavy doping of N-or P-type material may be produced by suitable adjustment of the impurity content of the atmosphere, and in those cases where there is a tendency to deposit some material as a noncrystalline layer, it is preferred to add a small percentage of HCl gas through valve 26 as an oxidizing gas to reoxidize non-epitaxially deposited material. The above process is illustrative of the processes available for depositing successive epitaxial layers

of different characteristics without the necessity for intervening manipulation of the substrate or exposure thereof to undesirable atmosphere or oxidations. The process is generally applicable to the controlled epitaxial deposits of silicon semiconductors and to semiconductors generally known as the III-V compounds as illustrated by gallium arsenide, indium phosphide and aluminum antimonide. Although the process as above illustrated utilizes chlorine as the halide of the reaction, it will be appreciated that other halogens may be used. Bromine is in some cases preferred and is suitable in both silicon and germanium technology.

The application of the above described electromagnetic radiation activated vapor growth process to the production of useful devices is illustrated in FIG. 2 wherein the sequential deposit of epitaxial layers is illustrated in the production of a transistor amplifier element with low resistivity regions thereof for lead attachment. A P-type crystal slice 41 shown in FIG. 2a, is subjected to growth of N-type material, as previously described in connection with FIG. 1, to produce to areas 31 and 32 as illustrated in FIG. 2b. The mask utilized to produce the layers in FIG. 2b is then changed to reduce the size of one of the areas and additional N-type material is deposited in areas 31 and 32 as shown in FIG. 2c. It is generally preferred to inactivate the light source 18 during this change over. The concentration of AsCl_3 impurity in the atmosphere is next increased and an additional layer of N+ germanium material is deposited through the same mask to produce areas 33 and 34 in the configuration of FIG. 2d. The light source 18 is again interrupted and a new mask inserted while the atmosphere in the furnace chamber 10 is changed from an AsCl_3 impurity to a BCl_3 impurity and a new area 35 of P-type epitaxial material is deposited on a portion of previously deposited N-type material to produce the transistor emitter configuration of FIG. 2e. The mask is again changed and the concentration of BCl_3 increased to deposit an area 36 of P+ germanium material on the P material just deposited, together with a region 37 of P+ material deposited upon the original P-type slice 41 producing the configuration of the FIG. 2f. The mask is again changed and additional region 37 P+ material is deposited to produce the configuration of FIG. 2g. The desired structure of the epitaxial layers has now been attained and the atmosphere within the chamber is now changed with the light source 18 turned off to produce a passivated film 38 on the crystal. This may be done by any conventional passivating procedure such as growth of an oxide film from oxygen or H_2O plus germanium tetrachloride containing atmosphere, or the deposit of an oxide such as SiO from a suitable decomposition process, as for example the decomposition of silanes. The passivating structure is thus produced as shown in FIG. 2h which may then be safely removed from the chamber and subsequently further processed to remove portions of the film 38 as shown in FIG. 2i for lead attachment and encapsulation.

The above illustration of the application of electromagnetic radiation activated epitaxial layer deposit is an example only of what may be accomplished, and variations in procedures will become obvious for the construction of other layered structures as desired.

I claim:

1. A method of vapor depositing an epitaxial layer of a material on a substrate, which comprises:
 - establishing a vapor atmosphere of the material to be deposited adjacent the substrate, maintaining the temperature of said substrate less than the temperature sufficient to effect epitaxial vapor deposition; and
 - focusing electromagnetic radiation on a localized area of the substrate in an effective amount to sustain epitaxial vapor deposition within said localized area.

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2. A method of vapor depositing an epitaxial layer of germanium on a substrate, which comprises:

establishing an atmosphere adjacent the substrate consisting essentially of GeCl_4 , GeCl_2 , H_2 , HCl and reaction products thereof;

heating the substrate to a temperature less than the temperature sufficient to effect epitaxial vapor deposition; and

focusing light energy on a localized area of the surface of the substrate in an effective amount to sustain epitaxial vapor deposition within said localized area.

3. A method of vapor depositing an epitaxial layer of material on a localized area of a substrate, which comprises:

placing the substrate in a heating chamber having a window therein with said area facing the window;

establishing a vapor atmosphere of the material to be deposited adjacent said area, heating said substrate to a temperature less than the temperature sufficient to effect epitaxial vapor deposition; and

focusing electromagnetic radiation through a mask outside the chamber, through the window, and onto said localized area of said substrate in an effective amount to sustain epitaxial vapor deposition within said localized area.

4. A method of vapor depositing successive areas of epitaxial material on a substrate, which comprises:

establishing a vapor atmosphere of the material to be deposited adjacent said substrate; maintaining the temperature of said substrate less than the temperature sufficient to effect epitaxial vapor deposition;

focusing light energy on a first localized area of the substrate in an effective amount to sustain epitaxial vapor deposition within said first localized area; and

subsequently focusing light energy on a second localized area of the substrate in an effective amount to sustain epitaxial vapor deposition within said second localized area.

5. A method of vapor depositing successive areas of a substrate of epitaxial material which comprises:

establishing a first atmosphere of a first material to be deposited adjacent said substrate; maintaining the temperature of said substrate less than the temperature sufficient to effect epitaxial vapor deposition;

focusing electromagnetic radiation on a first localized area of the substrate in an effective amount to sus-

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tain epitaxial vapor deposition within said first localized area;

reducing said radiation to less than said effective amount sufficient to sustain epitaxial vapor deposition;

establishing a second atmosphere of a second material to be deposited adjacent the substrate; and

focusing electromagnetic radiation on a second localized area of the substrate in an amount effective to sustain epitaxial vapor deposition within said second localized area.

6. The method of claim 5 wherein:

the first atmosphere consists essentially of a predominant quantity of a semiconductor material producing gas and a minor quantity of a first impurity producing gas sufficient to grow an epitaxial layer of a first conductivity type; and

the second atmosphere consists essentially of a predominant quantity of said semiconductor material producing gas and a minor quantity of a second impurity producing gas sufficient to grow an epitaxial layer of a second conductivity type.

7. The method of claim 6 wherein:

the first atmosphere consists essentially of germanium tetrachloride and a minor quantity of arsenic trichloride; and

the second atmosphere consists essentially of germanium tetrachloride and a minor quantity of boron trichloride.

8. The method of claim 2 wherein said light energy is of predominantly ultraviolet light.

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