

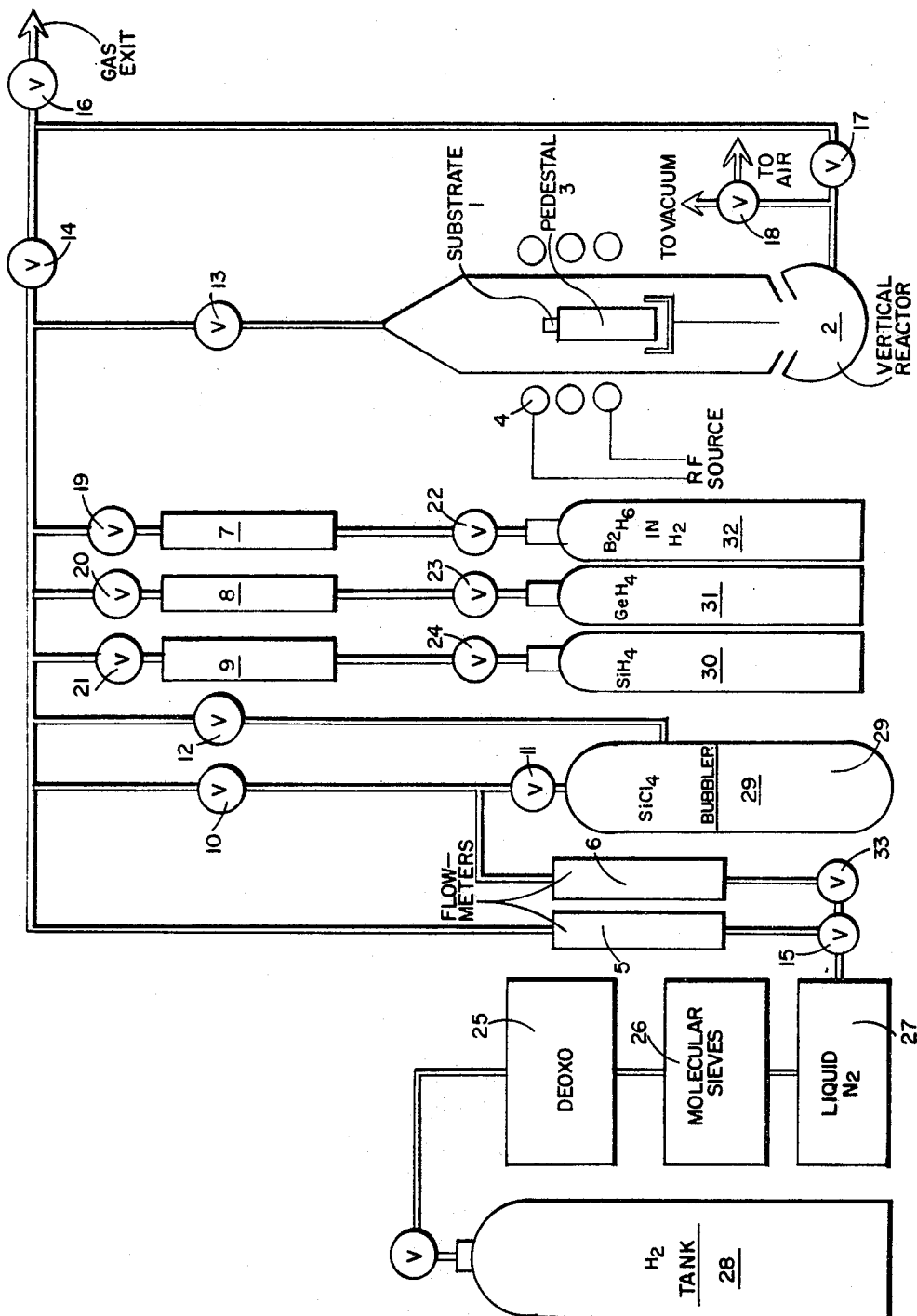
April 28, 1970

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3,508,962

EPITAXIAL GROWTH PROCESS

Filed Feb. 3, 1966



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3,508,962

EPITAXIAL GROWTH PROCESS

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Filed Feb. 3, 1966, Ser. No. 524,765

Int. Cl. C23c 11/00

U.S. Cl. 117—227

5 Claims

ABSTRACT OF THE DISCLOSURE

The invention is directed to a process for growing an epitaxial film on a single crystal substrate comprising the steps of forming initially an extremely thin film of semiconductor material on a desired substrate or surface by thermal decomposition of a hydride. Subsequently, a thicker film is deposited or grown on the thin film by thermally decomposing a halide in a hydrogen atmosphere or a mixture of halides and hydrides in a hydrogen atmosphere.

This invention relates to a process for improving the quality of a single crystal films grown on single crystal substrates.

Vapor deposition processes for depositing single crystal films on single crystal substrates often produce films of low quality. Defects in the substrate surface have a tendency to produce depositions with imperfections. The defects are more noticeable when thicker films are produced. Twinning in the deposited films also occurs more frequently when using existing deposition processes.

A process is needed whereby certain substrate surface defects can be tolerated and thick, high quality films can be produced with a minimum of twinning. Such a process would permit greater latitude in techniques of crystal growth when forming epitaxial films.

The improved process could also be useful in the formation of composites useful in the technology of translating devices, e.g. lasers, transistors, rectifiers, diodes, and other materials and devices associated with the field of microelectronics.

Therefore, it is an object of this invention to provide a process for producing thick, high quality single crystal films on single crystal substrates.

Another object of this invention is to produce single crystalline films on single crystalline substrates with a minimum of twin densities.

It is still another object of this invention to provide a process for improving the quality of thick single crystal films on single crystal substrates.

It is still a further object of this invention to provide a process for producing high quality single crystalline films on single crystalline substrates having some surface defects.

The invention in a particular embodiment may be characterized as a process for growing an epitaxial film on a single crystal substrate comprising the steps of forming initially an extremely thin film of semiconductor material on a desired substrate or surface by the pyrolysis (thermal decomposition) of a hydride. This step may be called the nucleation step. Subsequently, a thicker film is deposited or grown on the thin film by thermally decomposing a halide in a hydrogen atmosphere or a mixture of halides and hydrides in a hydrogen atmosphere. The materials are decomposed on the thin surface for such a period of time as required to produce a desired film thickness.

Each of the process steps has particular merits which when combined, results in producing a thick, high quality semiconducting film on a substrate.

The first step provides an extremely high density of

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discrete semiconductor nuclei which tend to agglomerate such that many surface defects, for example dirt, fine scratches, small substrate defects, etc. are eventually overcome by the rapidly growing film. Films thus nucleated have displayed twinned densities much less than films formed by halide nucleation. After the nucleation step, the remainder of the film is produced by thermal decomposition of materials exemplified herein.

These and other objects of the invention will become more apparent in connection with the following description and figures of which:

The figure is an illustration of the apparatus used in depositing the films on the substrate.

Referring now to the figure wherein substrate 1 is placed inside vertical reactor 2 on a pedestal 3 which is suspended in an area to be heated by coil 4. The coils are activated by an RF source (not shown). The system includes flow meters 5, 6, 7, 8 and 9 including valves 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24 and 33 for controlling the flow of material into and out of reactor 2. The system may also include deoxidizer 25, molecular sieves 26, and traps of liquid nitrogen 27. Other material sources such as a hydrogen source 28, silicon tetrachloride (SiCl_4) source 29, silane (SiH_4) source 30, germane (GeH_4) source 31, diborane (B_2H_6) in H_2 source 32 are also shown. Some of the materials may not be used in every process.

In depositing silicon, halides such as trichlorosilane, silicon tetrabromide, and silicon tetraiodide may be used as alternate silicon sources for the second step of the process. Higher hydrides of silicon such as Si_2H_6 may also be considered for use in the nucleation step 1.

In depositing single crystal germanium, germane (GeH_4) and germanium hydrides followed by germanium tetrahalides or trichloro germane in hydrogen may be used.

Substrate materials such as sapphire, beryllium oxide, magnesium oxide, silicon, germanium, chrysoberyl, calcium fluoride, Group II-V compounds, Group II-VI compounds, and others may be considered for single crystal deposits.

In the examples, it has been observed that the thickness of the film deposited in the nucleation step should be at least from 500 A. to 1,000 A. in thickness, whereas the total film deposited by thermal decomposition need only be limited by the thickness desired for use in a particular device. It was also observed in films investigated that the degree of microtwinning is related to the nucleation step and is relatively unaffected by the second step.

The invention is further described in the following examples of which:

EXAMPLE I

The sapphire substrate was placed on a pedestal inside a vertical reactor and heated by radio frequency to a temperature of approximately 1150°C . A silicon film was nucleated by 15–30 second pyrolysis of a 0.3 mole percent silane concentration in hydrogen flowing at about 3 liters per minute over the substrate. After a film having a thickness of between 500 and 1,000 A. was deposited, valves 21 and 24 were activated to cut off the silane source; and silicon tetrahalide was introduced into the hydrogen stream by manipulating valves 10, 11, 12 and 33 so that enough hydrogen was diverted through the SiSi_4 bubbler kept at a temperature of approximately 0° so that about 0.3 mole percent SiCl_4 passed into the reaction zone containing the substrate. For the conditions used, a silicon growth rate of about 0.3 micron per minute resulted.

Twin density comparison were made for different samples and orientations of sapphire substrates when the nucleation step was omitted. In the table, it is shown that

when the nucleation deposit was made using silane, the density of microtwins was significantly lower than the corresponding deposit using SiCl_4 only. Considering the total amount of deposited silicon as 100%, the percentages in the matrix column represent the untwinned material. The remaining material was divided among the four possible first order microtwins (T_1 - T_4) with respect to the primary orientation which can exist in silicon.

It should be understood that the substrate material does not necessarily have to be identical to the deposited semiconductor material, for example, germanium on silicon, boron on silicon, silicon on beryllium and other combinations may be used.

We claim:

1. A process for improving the quality of semiconductor epitaxial layers grown on single crystal substrates

TABLE I.—RELATIVE X-RAY INTENSITY DATA

Sample	Approximate substrate orientation	Deposit orientation	Relative depositing atmosphere	Matrix	T_1	T_2	T_3	T_4
A-----	1,102	(100)	SiCl_4 -----	81.62	11.00	2.28	3.38	1.22
B-----	1,102	(100)	SiCl_4 -----	76.31	14.22	9.46	-----	-----
C-----	1,012	(100)	Silane-----	99.15	.09	.29	.34	.13
D-----	1,102	(100)	do-----	98.86	1.73	1.41	-----	-----
E-----	1,123	(111)	SiCl_4 -----	65.79	.13	33.00	.42	.05
F-----	1,123	(111)	Silane-----	82.52	-----	17.17	.30	-----

EXAMPLE II

In a subsequent experiment, using the same apparatus and same general process steps, two polished sapphire (alpha-alumina) substrates cut from the same boule were placed individually in the vertical reactor 2 and heated as before. Two 6.6 micron films of silicon were grown; one by the use of silane and one by the improved two step process. The film formed by the two step process was more uniform in thickness and had the physical appearance of a better quality film. The two step process film had better reflectivity, surface structure, etc. as determined by test.

EXAMPLE III

In a subsequent example, using silicon as a substrate, the process as set forth in Example I was duplicated. The same general results were obtained.

EXAMPLE IV

In a subsequent example, using germanium as a substrate, and following the same process steps as outlined in Example I, germanium was deposited at 900° C. from germane (GeH_4) and then from germanium tetrachloride. The same results were obtained as before.

EXAMPLE V

In a subsequent example, using boron as a substrate, boron was formed from diborane (B_2H_6) as the nucleate material followed by additional boron formation from boron tribromide. The apparatus as described in Example I was used and the same general results were obtained.

Substrate materials as beryllium oxide, magnesium oxide, silicon, chrysoberyl, calcium fluoride, Group III-V compounds, Group II-VI compounds may also be used as substrate materials under proper substrate temperature conditions.

After the films are produced, semiconductor devices are fabricated in the films. It was determined by measuring characteristics of the produced semiconductor devices that the devices produced in films formed by the two step process have relatively improved characteristics over those produced in films from the one step process.

comprising the steps of forming a nucleation film of semiconductor material on a single crystal substrate by thermally decomposing a silane and depositing on said film a relatively thicker layer of silicon by thermally decomposing a silicone halide in a hydrogen atmosphere.

2. The process as recited in claim 1 wherein said substrate is selected from the class consisting of sapphire, beryllium oxide, chrysoberyl and silicon.

3. A process for improving the quality of semiconductor epitaxial layers grown on single crystal substrates comprising the steps of forming a nucleation film of semiconductor material on a single crystal substrate by thermally decomposing a germane and depositing on said film a relatively thicker layer of germanium by thermally decomposing a germanium halide in a hydrogen atmosphere.

4. The process as recited in claim 3 wherein said substrate is selected from the class consisting of sapphire, beryllium oxide, chrysoberyl, silicon and germanium.

5. A process for improving the quality of epitaxial layers grown on single crystal substrates comprising the steps of forming a nucleation film of semiconductor material on a single crystal substrate by thermally decomposing a boron hydride and depositing on said film a relatively thicker layer of boron by thermally decomposing a boron halide in a hydrogen atmosphere.

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U.S. Cl. X.R.

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